SOLUBILIZATION AND THERMAL PROPERTIES OF MICROEMULSIONS

BY

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To
My parents, my wife, and my daughter, Boram

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This work gave me a great opportunity to go one step further on my endless quest. I gratefully acknowledge those who have assisted me in this work.

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Abstract of Dissertation Presented to the Graduate School of
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SOLUBILIZATION AND THERMAL PROPERTIES
OF MICROEMULSIONS

By

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Chairman: Professor Dinesh O. Shah
Major Department: Chemical Engineering

The objectives of this study were to investigate the solubilization, interfacial tension and thermal properties of microemulsions as well as the excluded volume effect of a polymer in surfactant solutions.

Alcohol-free water-in-oil microemulsions using nonionic surfactants in place of short-chain alcohol were successfully formulated using Aerosol-OT, Arlacel 20, mineral oil and brine. The solubility of water in the microemulsion depended on the weight ratio of two surfactants. The oil displacement efficiency of the microemulsion was related to solubilization of the microemulsion and was greatest for the microemulsion having the largest solubilization resulting from the more piston-like displacement due to lower interfacial tension. Further, alcohol-free middle-phase microemulsion was successfully formulated using TRS10-80, Tween81, mineral oil and brine. Its solubilization and interfacial tension

were much larger and lower, respectively, compared to the corresponding middle-phase microemulsion containing n-butanol. The greater degree of solubilization, using the nonionic surfactant in place of the short-chain alcohol, was explained using the modified Winsor's R theory.

The mechanism of the excluded volume effect of anionic polymer on an anionic surfactant solution was studied using both static and dynamic light scattering techniques. The interfacial and surface tensions calculated by utilizing the light scattering data were in agreement with the experimental values supporting the excluded volume effect of polymer for the similarly charged polymer-surfactant solutions.

The effect of the structure of liquids on their thermal properties was studied using a transient method for thermal diffusivity developed in this study. An isotropic liquid showed 20% larger thermal diffusivity than a birefringent liquid, implying the significant effect of the microstructure of liquids on their thermal properties. As an extension, thermal conductivities of microemulsions were examined and were compared with the known equations for liquid mixtures. The results suggested that the microstructure of microemulsions influences the thermal properties of these systems.

The study of the phase stability of a methanol-isooctane-toluene mixture at -25 ^{o}C showed that alcohol and surfactants were effective in stabilizing the mixture as a single phase at -25 ^{o}C and

their effectiveness decreased in the following order: mixture of anionic surfactant and alcohol > anionic surfactant > alcohols.

CHAPTER 1

INTRODUCTION

Since 1943, when Hoar and Schulman (1) first described a microemulsion as a transparent or translucent system formed spontaneously upon mixing oil and water with a relatively large amount of ionic surfactant together with a cosurfactant such as an alcohol of medium chain length (C_4 to C_7), extensive studies have been done on the surfactant solutions and the microemulsions because of their usefulness in numerous applications such as tertiary oil recovery, detergency, catalysis, drug delivery, lubrication, and so on. Numerous books, symposium proceedings and review articles have been published during the past decade (2-15), and it is virtually impossible to review all such studies here. Hence, this chapter will focus only on the fundamental concepts and findings which are related to the subjects of this dissertation, such as solubilization, interfacial tension, oil displacement, interaction between surfactants and polymers, thermal conductivity, and phase stability.

1.1 Surfactants, Micelles and Microemulsions

Surfactants are amphiphatic molecules having distinct hydrophobic and hydrophilic groups (16). Depending on the chemical structure of the polar group, surfactants can be nonionic, cationic,

anionic, or zwitterionic. The nonpolar part of surfactants can be a saturated or unsaturated, straight, branched or cyclic hydrocarbon or can be one or more hydrocarbon chains. Functional groups can also be incorporated into surfactants. The structures of typical surfactants are shown in Figure 1-1.

When surfactant molecules are dissolved in water, the presence of the hydrophobic group of a surfactant molecule in the interior of water causes a distortion of water structures increasing the free energy of the system. This means that less work is needed to bring a surfactant molecule than a water molecule to the surface, since the presence of the surfactant decreased the work needed to create a unit area of surface (16).

On the other hand, the presence of the hydrophilic group of a surfactant molecule prevents the surfactant from being expelled completely from water as a separate phase, because that would require desolvation of tbe hydrophilic group. Therefore, the amphiphatic structure of a surfactant molecule causes not only concentration of the surfactant at the surface and reduction of the surface tension of water, but also orientation of a surfactant molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from the aqueous phase (17).

The properties of a surfactant are determined by the balance between its hydrophobic and hydrophilic groups. If the hydrophilic group is dominant, the surfactant is called a water soluble surfactant because the hydrophilic group drags the entire surfactant

Anionic Surfactant

$$R C_6 H_4 S O_3^- Na^+$$

(Alkylbenzene Sulfonate)

Cationic Surfactant

$$R N H_3^+ Cl^-$$

(Salt of a Long-Chain Amine)

Zwitterionic Surfactant

$$R \overset{+}{N}(CH_3)_2 CH_2 CH_2 SO_3^-$$

(Sulfobetaine)

Nonionic Surfactant

$$R C_6 H_4 (O C_2 H_4)_X O H$$

(Polyoxyethylenated Alkylphenol)

Figure 1-1. Structure of typical surfactants. R represents alkyl chain of C_{12} to C_{18} methylene groups.

molecule in water. In contrast, if the hydrophobic group is dominant, it does not dissolve in water. The lowering in surface (or interfacial) tension as mentioned earlier can be described by the well-known Gibbs adsorption isotherm for a multiple-component system as (18)

$$d\gamma = -\Sigma\, \Gamma_i\, d\mu_i = -\Sigma\, \Gamma_i\, RT\, d(\ln a_i) \qquad (1\text{-}1)$$

where γ is the surface tension (or interfacial tension), Γ_i is the surface excess of component i (amount of component i adsorbed per unit area), μ_i is the chemical potential of component i, and a_i is the activity of the component i. Equation 1-1 basically states that the increase of surfactant activity a_i in the solution would result in a decrease of surface tension (or interfacial tension) if the surface excess of the surfactant is positive.

As the concentration of a soluble surfactant in water gradually increases, the monomer concentration in water and the surface concentration of adsorbed surfactant increase. At a critical bulk concentration of surfactant, known as the critical micelle concentration (cmc), the surfactant molecules start to form the aggregates in water called micelles. In general, the micelles are spherical aggregates of surfactant molecules 40-100 $\mathring{A}$ in diameter and are in equilibrium with single surfactant molecules or monomers (19). At cmc, the solution properties such as osmotic pressure, surface tension, viscosity, electrical conductivity, and density abruptly change (20).

Properties of aqueous micelles, in aquesous solutions have been discussed in detail in several books and reviews (8, 21-33). The formation of micelles in an aqueous solution creates a local nonpolar environment at the cores of micelles within the aqueous phase as shown in Figure 1-2 (a) because the hydrophobic group of a surfactant molecule tends to move away from water. Oil soluble molecules can be dissolved within the micelles (19, 29, 34). As shown in Figure 1-2 (b), the structure of the micelle in a nonpolar solution is similar to that of the micelle in an aqueous solution but reversed, with the hydrophilic groups and water comprising the interior region surrounded by an outer region containing the hydrophobic groups and solvent molecules (35).

It should be noted that the exact molecular structure of the micelles is still disputed even though the structure of the micelle in an aqueous solution, at concentrations not too far above the cmc, is generally considered to be roughly spherical (17, 36). For example, Rouviere et al. (37) proposed a spherical shape of the reversed micelle to explain the observed effects of electrolytes on solubility of water, relative viscosity, and enthalpy of hydration in Aerosol-OT-n-decane system while Ekwall et al. (38) showed evidence for prolated ellipsoidal Aerosol-OT reversed micelles. Further, as shown in Figure 1-3, the structure of the micelle changes from spherical through rod- or disklike to lamellar in shape with changes in temperature, concentration of surfactant, and appropriate additives (19, 39). It should be also noted that the

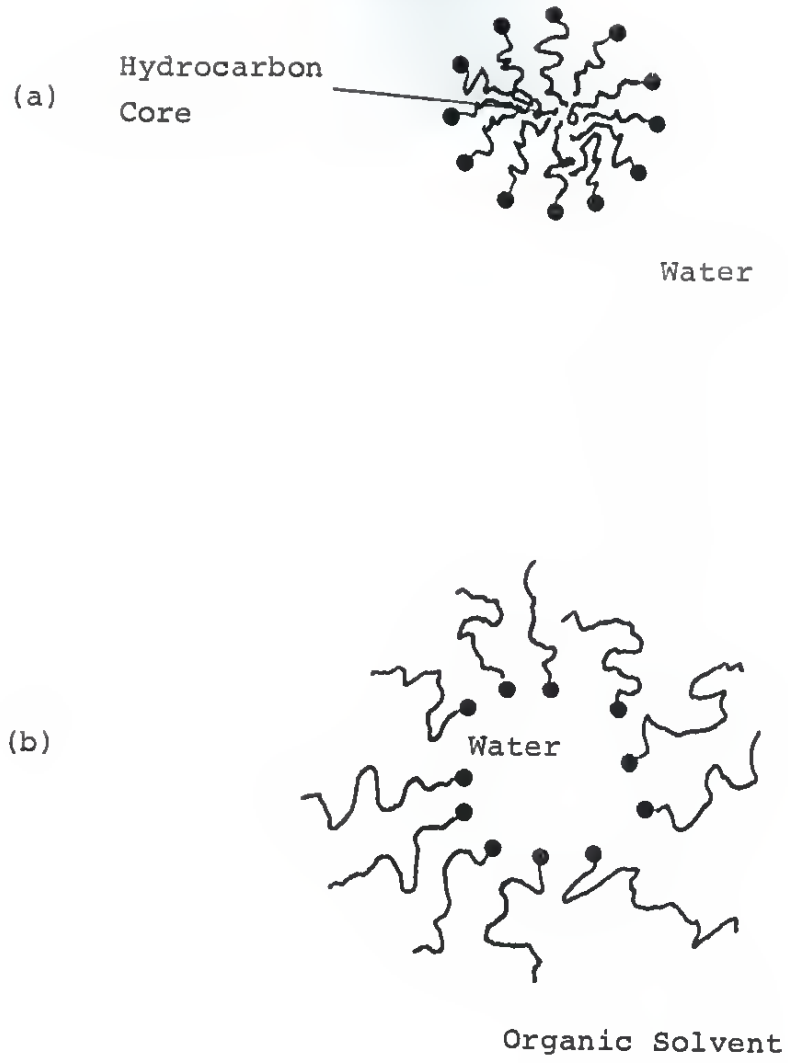


Figure 1-2. Two typical micelle types. (a) Normal micelle; (b) reverse micelle.

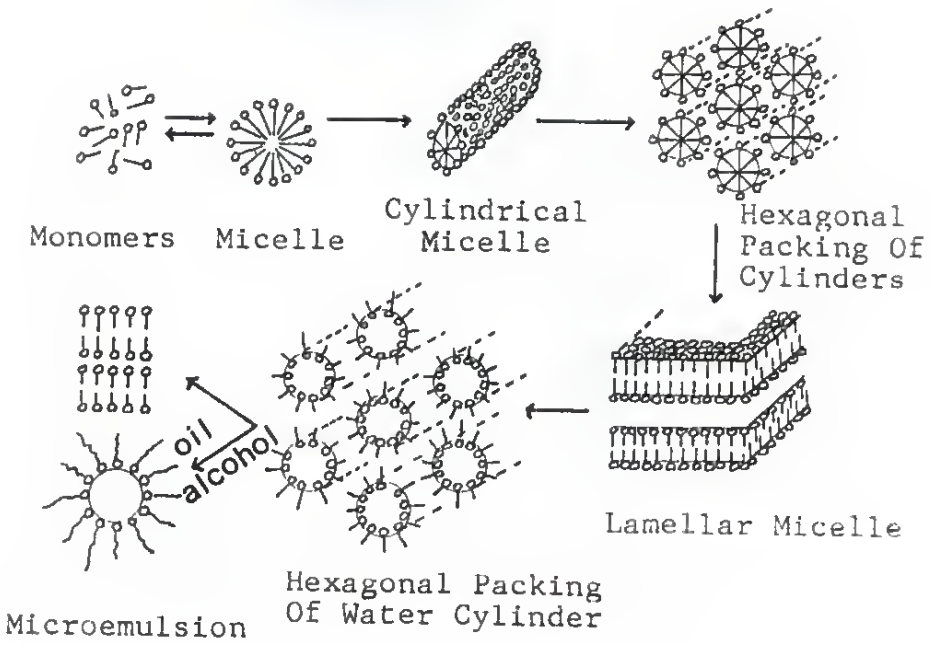


Figure 1-3. A schematic presentation of structure formation in surfactant solution upon the concentration of surfactant as well as physico-chemical conditions.

equilibrium between single surfactant molecules (monomers) and micelles at the concentrations beyond the cmc is not static but dynamic as shown in Figure 1-4. The dynamic aspect of the equilibrium has been reviewed in the previous two review articles on amphiphile aggregation in water (32) and in nonpolar solvent (40) in addition to a recent Ph.D. dissertation (33). The chain packing in mecelles have been also studied in recent years using the statistical thermodynamics of molecular organization and the conformational statistics of the hydrocarbon chains within the hydrophobic core (25, 26, 27). The results may be summarized as follows: Micellar aggregates are charcterized by motions occurring on distinctively different time scales. The fast motions are characterized by correlation times of the order of 20 ps (slightly different at different positions along the chain). These correlation times are close to those of the corresponding liquid alkanes. The slow motion for spherical micelles can be accounted for by micelle rotation and surfactant molecule lateral diffusion. The experimental results by the measurements of free energies of transfer of nonpolar molecules and surfactant molecules into micelles, viscosity and diffusion measurements, nmr relaxation measurements and neutron diffraction studies suggest minimal water penetration in micellar cores (27, 28).

Many micellar solutions can spontaneously solubilize large amounts of oil (or water) to form microemulsions (41). At present, there is not a precise, or indeed agreed upon, definition of microemulsions (8, 10, 42-44). Recently, Shinoda and Lindman wrote

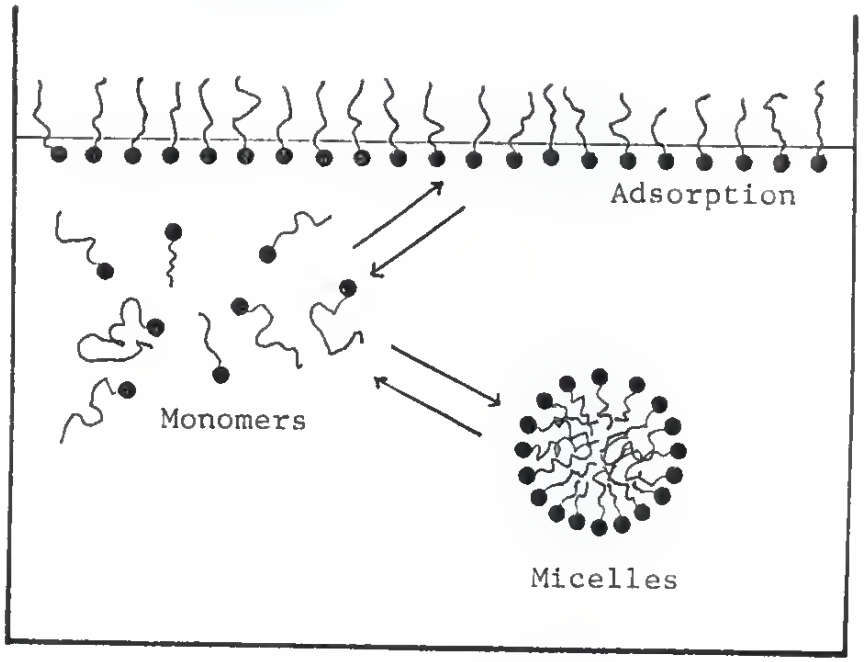


Figure 1-4. A schematic presentation of the dynamic equilibrium between surfactant monomers, micelles and adsorbed monolayer.

in a review article: "In a strict sense, a microemulsion may be defined as a system of water, oil, and amphiphile(s), which is a aingle phase, and a thermodynamically stable isotropic solution. In a wide sense, it has been used to include fairly stable dispersions which are transparent, translucent (opalescent), and opaque, but it appears that serious confusion may arise without a clear distinction between thermodynamically stable and unstable systems (even if the difference in free energy may be extremely small)" (15, p.136).

In spite of the controversy about the definition of microemulsions mentioned above, the designation of a clear isotropic single-phase region in a phase diagram as microemulsions does offer practical convenience in terminology (33). Another controversy regarding the nature of microemulsiona is a distinction between micelles and microemulsions. One group of investigators (13, 45) believes microemulaions to be special types of micellar solutions, that is, microemulsions to be solutions of swollen micelles of emulsifying agent in the interior of which the dispersed liquid is solubilized.

In contrast, a aecond group of researchers (46, 47) believes that micelles and microemulsions are fundamentally different. They feel that the relatively small size of micelles precludes them from having properties and characteristics of the dispersed aggregates in microemulsiona and conaider microemulsions to consiat of 10-200 nm diameter droplets of the diapersed liquid surrounded by an interfacial film in which the emulaifying agent molecules outnumber

oil molecules (48). In either case, the emulsifying agent is oriented in such a fashion that the hydrophobic groups face the oil phase and the hydrophilic groups face the aqueous phase. Water-in-oil (w/o) microemulsions may be considered either as micellar solutions containing reverse micelles with water solubilized in the inner core or as emulsions containing tiny droplets of water surrounded by an interfacial film. Oil-in-water (o/w) microemulsions may be thought of either as micellar solutions containing normal micelles with solubilized oil in their inner cores or as tiny droplets of oil surrounded by an interfacial film dispersed in water.

In addition to the o/w and w/o type microemulsions, a bicontinuous structure has been proposed which does not have a distinct dispersed or dispersing phase (49, 50). Whether the microemulsion will be w/o or o/w depends on the direction of curvature of the interfacial region as determined by such factors as the difference in interfacial tension (51), or interfacial pressure (52), on the two sides of the interface, and/or the difference in volumes and compressibilities of the hydrophilic and hydrophobic moieties of the surfactants (53). For example, if the oil-hydrophobic end tension were greater (or interfacial pressure lower) than the water-hydrophilic end tension, then the former side would be shortened, causing the interfacial film to be concave toward the oil, resulting in the enclosure of the oil by the water and therefore forming an o/w microemulsion. A preferentially oil-soluble surfactant would produce a lower interfacial tension (or greater

interfacial pressure) at the oil interface, yielding a w/o microemulsion while a preferentially water-soluble surfactant would produce a lower interfacial tension (or greater interfacial pressure) at the water interface, yielding an o/w microemulsion (17).

Such an explanation of the formation of the o/w- or w/o microemulsion is consistent with the geometrical packing considerations of surfactants through the direction of curvature of the interfacial film. The latter describes the geometrical packing of surfactants at the interface by the packing ratio of cross-sectional area of hydrocarbon chain to that of polar head of a surfactant molecule at the interface, $V/a_o\ l_c$, where V is the volume of hydrocarbon chain of the surfactant, a_o is the optimal cross-sectional area per polar head in a planar interface, and l_c is approximately 80-90% of fully extended length of the surfactant chain (54). As shown in Figure 1-5, it is intuitively clear that a smaller cross-sectional area of tail than that of head ($V/a_o\ l_c < 1$) will favor the formation of the o/w microemulsion (Figure 1-5a), while a greater cross-sectional area of tail than that of head ($V/a_o\ l_c > 1$) would favor the w/o microemulsion (Figure 1-5c). A planar interface requires $V/a_o\ l_c = 1$ which leads to the formation of lamellar structure (Figure 1-5b). This geometrical packing consideration has been well reviewed in a previous publication (33).

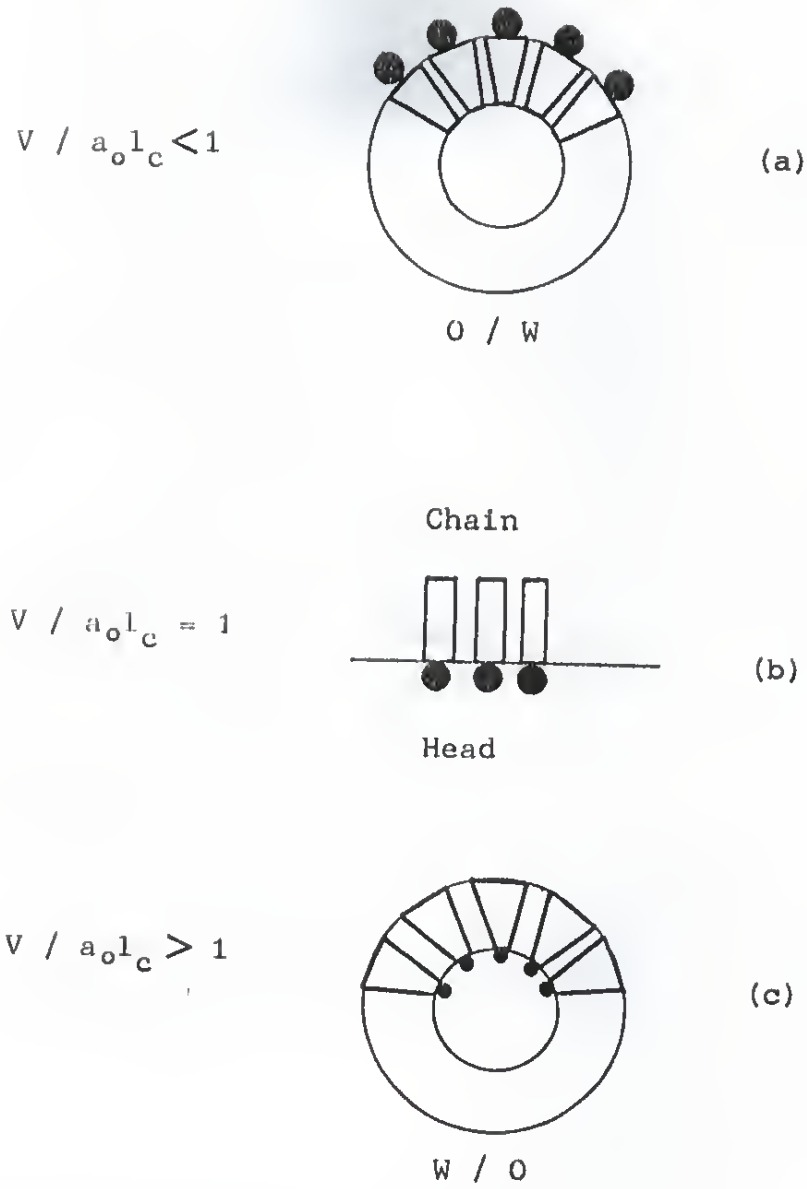


Figure 1-5. A schematic diagram representing the effect of the geometrical packing of surfactants on the structure of microemulsions. (a) Oil-in-water microemulsion (head area > chain area); (b) lamellar structure (head area= chain area) (c) water-in-oil microemulsion (head area < chain area).

1.2 Solubilization in Microemulsions

One of the important properties of micelles and microemulsions is the ability to solubilize a solvent-insoluble substance, important from a practical point of view because most industrial applications originate from thia property (e.g. paints, inks, etc.).

Correlations between the chemical structure of a surfactant and its solubilization capacity are complicated by the fact that both phases, oil and water, can have variable compositions. Moreover, the concentration at which the surfactant is used determines its solubilization capacity as well as the type of microemulsion (o/w or w/o) formed. Consequently, such complexity makes it difficult to select the proper surfactant for a given purpose. However, there are some general guidelines (17) that can be helpful in the selection of surfactants: 1) Surfactants must show surface activity and produce a low interfacial tension in the particular system in which it is to be used; 2) surfactants must form, at the interface, either by itself or with other adsorbed molecules that are present there, an interfacial film that is condensed because of lateral interactions between the molecules comprising the interfacial film; 3) surfactants must migrate to the interface at a rate such that the interfacial tension is reduced to a low value in the time during which the microemulsion ia being produced; 4) preferentially water soluble surfactants form o/w microemulsions; 5) preferentially oil soluble surfactants form w/o microemulsions; 6) the more polar the oil phase, the more hydrophilic the surfactant should be; 7) the

more nonpolar the oil to be solubilized, the more hydrophobic the surfactant should be.

A practical way to select the proper surfactant is the HLB (Hydrophile-Lipophile Balance) method. In the HLB method (55), a number between 0 and 40 is assigned to a surfactant depending on its solubilization behavior and is related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the surfactant molecule. The smaller the HLB value is, the more hydrophobic the aurfactant is. An HLB value of 10 is assigned to the balanced state between the hydrophilic and hydrophobic portions of the surfactant molecule. In addition, a similar range of numbers has been assigned to various substances that are frequently solubilized such as oils, paraffin wax, xylene, and so on (56). Thus, the surfactant is selected whose HLB number is approximately the same as that of the ingredient to be solubilized. However, since the chosen HLB value can be obtained by a combination of the surfactants using the weighted average HLB number, various combinations of surfactants with the same weighted average HLB number must then be tried to determine the optimum aurfactant combination.

Winsor's R-theory of solubilization (57) is also helpful in selecting the proper surfactants for maximum solubilization under the given conditions. Since this will be explained in detail in a later chapter, it will be sufficient here to mention that this theory qualitatively considers the interaction energies between the surfactant and oil and between the surfactant and water. As

described later, the magnitudes of the two interaction energies are related to the solubilization capacity of the microemulsion.

So far, the discussion has focused on the macroscopic view of solubilization. Therefore, considering the microscopic view of solubilization will further help us to understsnd the solubilization in the microemulsions. From studies on the solubilizate before and after solubilization using X-ray diffraction (58, 59), ultraviolet spectroscopy (60) and nmr spectrometry (61, 62), it haa been known that the site of the micelle at which aolubilization occurs varies with the nature of the material solubilized. Figure 1-6 shows the five sites available for solubilization based on these findings: 1) on the surface of the micelle, at the micelle-solvent interface; 2) between the hydrophilic head groups; 3) in the so-called pslisade layer of the micelle between the hydrophilic groups and the first few carbon atoma of the hydrophilic groups that comprise the outer core of the micelle; 4) more deeply in the palisade layer; and 5) in the inner core of the micelle.

In squeous solvents, nonpolar hydrocarbons are solubilized in the inner core of the micelle, between the ends of the hydrophobic groups of the surfactant molecules. Polarizable hydrocarbons have been ahown to be solubilized in quaternary ammonium solutiona initially by adsorption at the micelle-water interface, replacing water molecules that may hsve penetrated into the outer core of the micelle close to the polar heads, but solubilization of additional material is either deep in the palisade layer or located in the inner core of the micelle (63). In aqueous medium, large polar

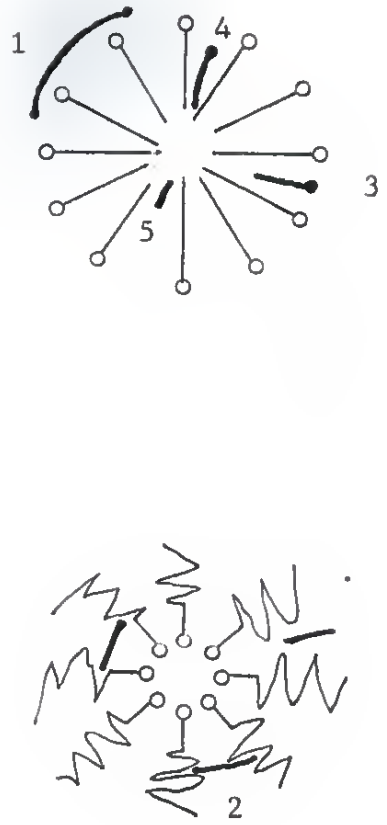


Figure 1-6. Sites of solubilization of material in a surfactant micelle. (1) On surface of micelle; (2) between the head groups; (3) in palisade layer; (4) more deeply in palisade layer; (5) in the inner core of the micelle.

molecules are believed to be solubilized between the individual molecules of surfactant in the palisade layer with the polar groups of the solubilizate oriented toward the polar groups of the surfactants and the nonpolar portiona oriented toward the interior of the micelle. Small polar molecules, in aqueous medium, are generally solubilized close to the surface in the palisade layer or by adsorption at the micelle-water interface. Among the sites mentioned above, the solubilization in the inner core of the micelle is relevant to the formation of microemulsions (17) even though other sitea may be considered (64).

It is easy to see the relationship between solubilization and the drop size of a microemulsion by considering a simple geometric calculation for a sphere:

$$V = A_t R / 3 \qquad (1\text{-}2)$$

where A_t is the total interfacial area, R is the radius of the droplet, and V is the total solubilization volume in a microemulsion drop. Since A_t is related to the total emulsifier concentration in a system, the aolubilization is directly related to the droplet radius and hence the curvature of the interface (65-70). The radius of the microemulsion droplet is related to the thermodynamic stability of microemulsions. This ia evident from the observation that all microemulsiona exhibit phase separation beyond a critical radius of droplets depending on the composition of the system.

It has been known that the free energy of a microemulsion is primarily determined by the entropic contribution of the dispersion of the droplets in the continuous phase, the interfacial contribution (including the curvature effect) and the interaction between droplets (69, 71-73). Among these three contributions to the free energy of a microemulsion, the curvature of interface and the interaction between droplets are known to be strongly influenced by the molecular structures of the interfacial layer and the continuous phase (64, 74). These two effects on the stability of the w/o microemulsion droplets were recently studied by Hou and Shah (75). Their theoretical and experimental results can be summarized as follows: 1) From the consideration of the stability of microemulsion systems, the growth of microemulsion droplets during the solubilization process has to be limited either by the radius of the spontaneous curvature of interface (R_o) as the result of curvature effect, or by a critical radius of droplets (R_c) due to the attractive interaction among the droplets; 2) for the systems where solubilization capacity of water is limited by the spontaneous curvature of the layer, the solubilization capacity can be increased by any modification of the molecular structure of either interface or continuous phase so that the spontaneous curvature of the layer is decreased (i.e., R_o is increased); 3) for the systems where the solubilization capacity is limited by critical droplet radius, the reduction of attractive interaction among droplets (i.e., increase of R_c) increases the solubilization capacity of water; 4) both R_o

and R_c are strongly influenced by the variation of the molecular structure of interface and continuous phase; 5) the maximum solubilization can be obtained by changing the molecular structure of interface or continuous phase, as a result of the compromise between the two opposite effects of the curvature of interface and the attraction among droplets.

From the above mentioned macro- and microscopic view, it is clear that the two important factors for the large solubilization in the microemulsion are the hydrophilic and lipophilic balance of the surfactant and the stability of the microemulsion droplets. Both factors are strongly affected by the structure of the surfactant and the solvent.

1.3 Oil Displacement by Surfactants

When a new oil reservoir is discovered, the reservoir usually possesses the natural pressure to move the oil to the production wells by expansion of volatile components. This phase is called primary oil recovery. When the natural pressure decreases, it is necessary to increase the pressure by injection of water. The injection of water, called secondary oil recovery or water flooding, is stopped when the production cost becomes significant compared to the value of the produced oil. The total oil recovery by the primary and secondary oil recovery is less than 40% of the original oil in place. Therefore, the remaining oil, 60%, is the target of the enhanced oil recovery techniques called tertiary oil recovery. There are several proven techniques for such tertiary oil recovery:

surfactant-polymer flooding (76-78), foam flooding (78-80), CO_2 flooding (81), caustic aolution flooding (82), steam injection (83), thermal combustion (84), and microbial methods (85). This section focuses on the fundamental aspecta of the surfactant-polymer flooding (or microemulsion flooding) as well as related phenomena.

The use of a microemulsion to displace the residual oil in the reservoir was not initiated until representatives of the Marathon Oil Company presented four technical papers at the annual fall meeting of the Society of Petroleum Engineers in 1967. Since then many researchera have proposed optimal microemulsion systems for given reservoir conditions. Today, enhanced oil recovery by microemulsions has become one of the most studied applications of microemulsion technology.

Because of multicomponents and multiphases involved in tertiary oil recovery by microemulsions, most of the studies have been experimental rather than theoretical. Further, most of the studies have been done on the laboratory scale, because a study on a pilot plant scale requires considerable expense and several years to obtain data. Nevertheless, many important findings of the laboratory scale studies help ua to understand the mechanism and the effect of several variables on the enhanced oil recovery by microemulsions. A few field testa for surfactant-polymer flooding have been reported (76, 77). The result showed that aurfactant-polymer flooding increased tertiary oil recovery by 4 times compared to polymer flooding (77).

1.3.1. The Importance of Low Interfacial Tension

The fundamental question of why a microemulsion is effective for the tertiary oil recovery can be answered by considering the forces acting on the residual oil drops and the concept of capillary number.

After the water flooding, the residual oil drops are captured in the porous medium by the capillary force. In a dynamic situation, the residual oil drop is also subjected to a viscous force. The ratio of viscoua force to capillary force is defined as the capillary number, even though the detailed variables of the capillary number are somewhat different depending on the investigators (86). Foster (87) has defined the capillary number as

$$N_{ca} = \eta V/\gamma\phi \qquad (1\text{-}3)$$

where η and V are the viscosity and velocity of the displacing fluid, respectively. Gamma is the interfacial tension and ϕ is the porosity of the poroua medium. He found, as shown in Figure 1-7, that the level of the residual oil decreased as the capillary number increased. Others alao have shown similar results (86). Since the capillary number after the water flooding is around 10^{-6}, it should be increased by 3 to 4 orders of magnitude for enhanced oil recovery (88-91). Thua, it is obvious from the definition of the capillary number that a decrease in the interfacial tension increases the capillary number. Therefore, the lowering of the interfacial

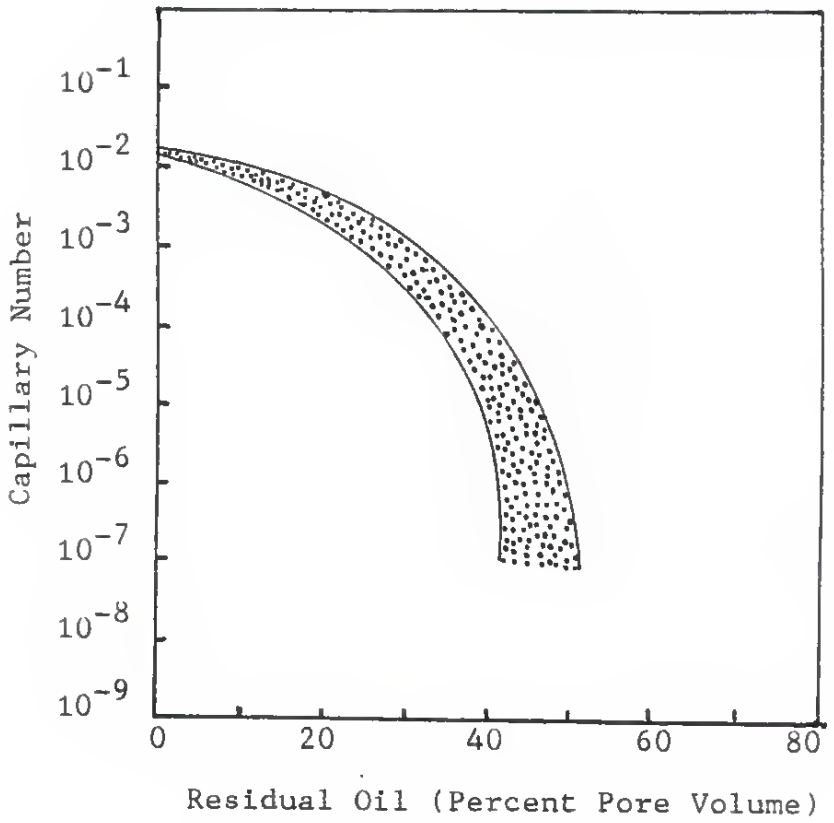


Figure 1-7. Dependence of residual oil saturation on capillary number.

tension is believed to be a major role of a microemulsion for tertiary oil recovery. A microemulsion can decrease the interfacial tension from 20 or 30 dynes/cm (mN/m) to 10^{-3} dynes/cm (mN/m), resulting in the mobilization of the oil drops trapped after water flooding.

1.3.2. Application of Microemulsions in Tertiary Oil Recovery

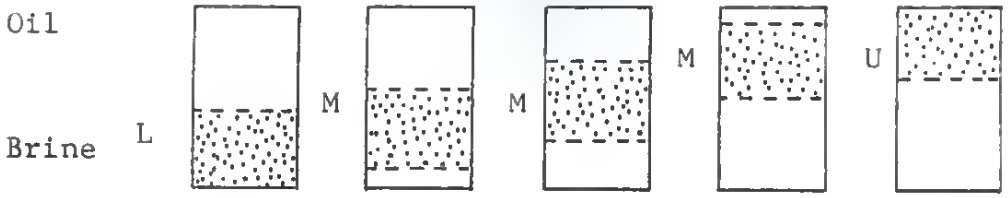
The application of microemulsions to tertiary oil recovery was well described by Healy and Reed (92). In this process, a microemulsion or a surfactant slug is injected into a porous medium after the water flooding. The slug is then displaced by thickened or viscous water (usually a polymer solution). As long as the slug has compositions within the single-phase region, oil is displaced miscibly and all of it is recovered. However, for economic reasons, the small size of the slug is mixed with the residual oil and brine resulting in the two or more phases. From this point, the displacement is immiscible and less efficient, and some of the residual oil remains trapped in the pores. The phase change of the microemulsion slug during tertiary oil recovery is correlated to the phase behavior studies in the test tubes (93). Several investigators (94-99) showed that tertiary oil recovery could be predicted using a chemical flooding compositional simulator based on the phase behavior of a surfactant, an alcohol, oil and brine.

1.3.3. Optimization of Microemulsions for Tertiary Oil Recovery

Several controlling factors are involved in tertiary oil recovery by microemulsions, namely, interfacial tension,

solubilization, coalescence and mobility control (100). Therefore, these factors should be considered to optimize microemulsions for tertiary oil recovery. Furthermore, a middle-phase microemulsion has received more attention than lower- and upper-phase microemulsions due to its greater solubilization capacity and lower interfacial tension at both microemulsion/oil and microemulsion/water interfaces. Therefore, this section will be devoted to the phenomena occurring in such a middle-phase microemulsion aystem.

The Concept of the Optimal Salinity. When a microemulsion is formed by mixing oil and brine with a surfactant and an alcohol in a tube, the location of the microemulsion phaae in a vertical tube varies depending on several parameters as shown in Figure 1-8. The typical way to see the phase behavior is to increase the concentration of salt while other parameters are fixed. As the concentration of salt increases, the location of the microemulsion phase moves from the bottom to the top through the middle of the vertical tube; consequently, a lower-phase, an upper-phase, and a middle-phase microemulsion have been named. The lower-phase and the upper-phase microemulsions are o/w- and w/o type, respectively, while the structure of the middle-phase microemulsion has not yet been clearly known (100). A typical definition of the optimal salinity is the aalinity at which the volumes of oil and brine solubilized in the middle-phase microemulsion are equal (101).



The Transition L ⟶ M ⟶ U Occurs By:

1. Increasing Salinity
2. Decreasing Oil Chain Length
3. Increasing Alcohol Concentration (C_4-C_6)
4. Decreasing Temperature
5. Increasing Total Surfactant Concentration
6. Increase Brine/Oil ratio
7. Increasing Surfactant Solution/Oil Ratio
8. Increasing Molecular Weight Of Surfactant

Figure 1-8. Schematic illustration of the factors influencing the transition from the lower- to the middle- to the upper phase microemulsion.

Another definition is the salinity at which the least amount of surfactant and/or alcohol is required to form a single phase (the ratio of surfactant to alcohol is fixed) (102). The optimal salinities obtained by these two different definitions are similar. The importance of the optimal salinity lies in the fsct that the interfacial tension is lowest for a microemulsion with excess oil or brine phase at the optimal salinity (103-107). Thus, the optimal salinity can serve as a parameter to formulate an optimal system which produces ultralow interfacial tension.

An important relationship was proposed by researchers (71, 108): the interfacial tension and the solubilization parameter are inversely related at optimal salinity as

$$\frac{\bar{\gamma}\bar{\sigma}}{\text{Cos}\,\pi\ /\ 4} = \text{constant} \qquad (1\text{-}4)$$

where $\bar{\gamma}$ is the interfacial tension at optimal salinity and $\bar{\sigma}$ is the solubilization parameter at optimal salinity (the solubilization parameter is the volume of oil or brine solubilized in the microemulsion phase per unit volume of surfactant). Equation 1-4 implies that a low interfacial tension requires a large solubilization of oil or brine in the microemulsion phase. Bourrel and Chambu (102) discussed the rules to achieve high solubilization by considering interaction energies among molecules of oil, brine and surfactants (and alcohols). One of their conclusions was that the interaction energy between brine and surfactants should be

equally balanced with the interaction energy between oil and surfactants for an optimal system. Further, they showed that aolubilization depends on the magnitude of interaction energies for an optimal syatem. Hsieh and Shah (109) ahowed the effect of chain length of oil and alcohols, and the surfactant to alcohol ratio on the optimal salinity. They found that for the same concentration and type of petroleum sulfonate and alcohol, the optimal salinity of the microemulsion system can be predicted from the density of the n-alkane. The phenomena occurring at optimal salinity are summarized in Figure 1-9 (107).

Coalescence Process. While ultralow interfacial tension is required to mobilize oil drops trapped in porous media, coalescence of the mobilized oil drops is necessary to form an oil bank. Hence very low interfacial viscosity is desirable to form an oil bank (107). Figure 1-10 shows the role of low interfacial viscosity in microemulsion flooding. A previous study (110) showed that tertiary oil recovery efficiency was almost directly correlated with coalescence rate for the system studied. Vijayan et al.(111) showed that minimal phase aeparation time or the fastest coalescence rate of emulsions occurred at optimal salinity. Figure 1-11 shows a correlation between the coalescence rate in emulsions and apparent viscosity in the flow through porous media. The minimal apparent viscoaity for the flow of emulaions in porous media coincides with minimal phase separation time at the optimal salinity. This

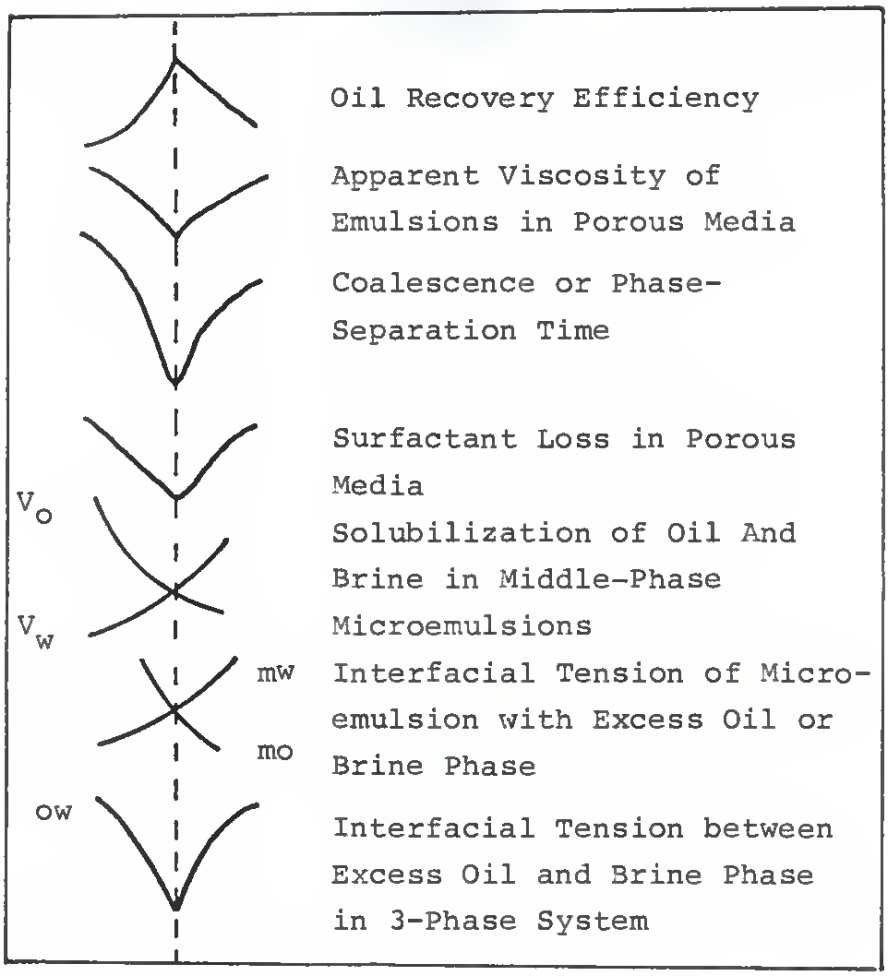

Oil Recovery Efficiency
Apparent Viscosity of Emulsions in Porous Media
Coalescence or Phase-Separation Time
Surfactant Loss in Porous Media
V_o
Solubilization of Oil And Brine in Middle-Phase Microemulsions
V_w
mw
Interfacial Tension of Micro-emulsion with Excess Oil or Brine Phase
mo
ow
Interfacial Tension between Excess Oil and Brine Phase in 3-Phase System
Optimal Salinity
Salinity

Figure 1-9. The phenomena occurring at the optimal salinity.

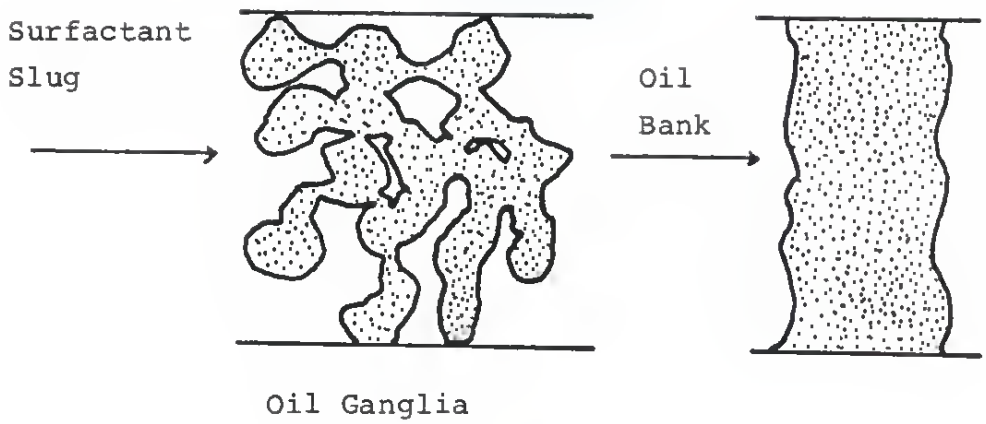


Figure 1-10. The role of low interfacial viscosity in promoting coalescence of oil ganglia.

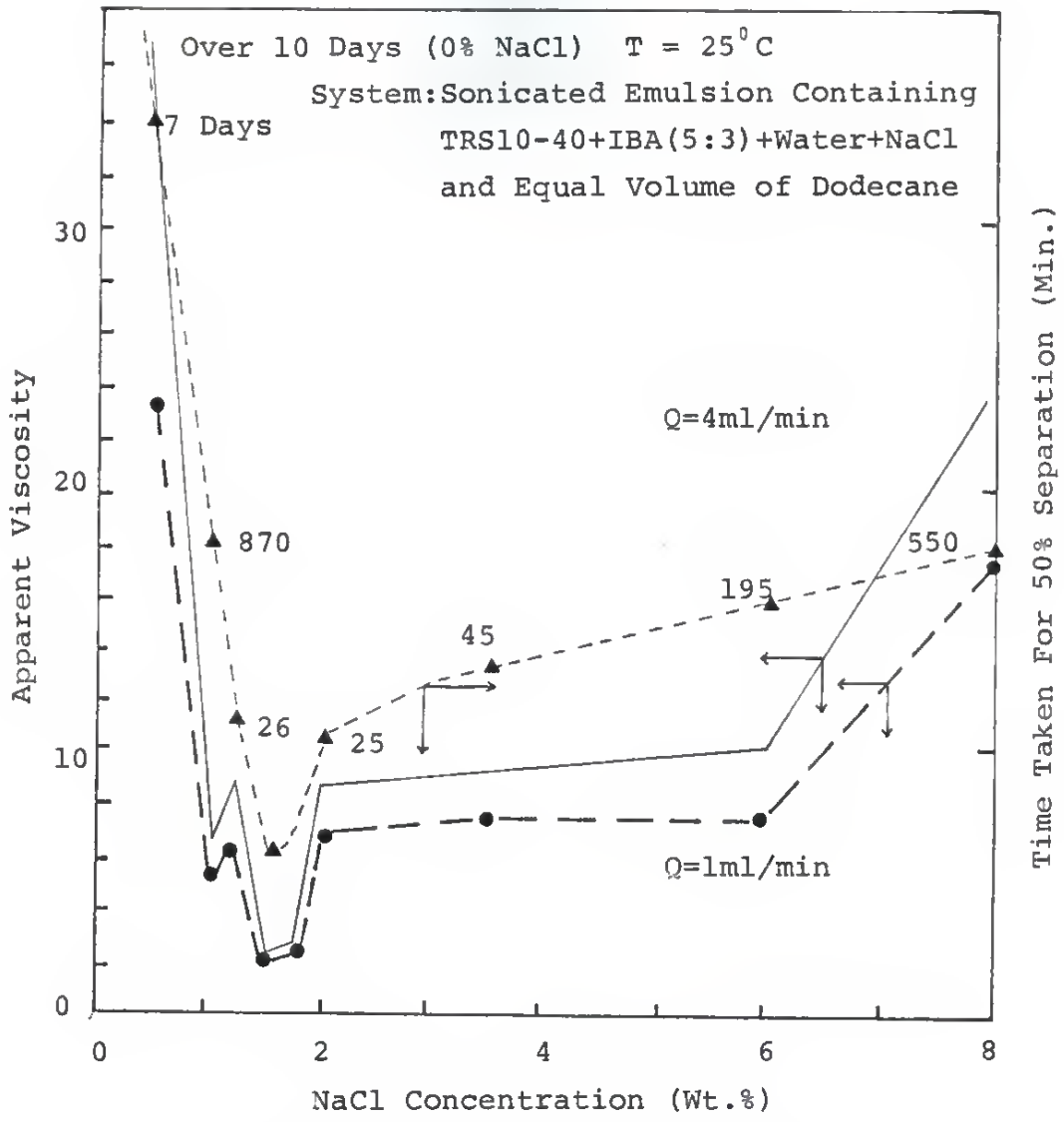


Figure 1-11. Correlation between the apparent viscosity and coalescence rate of sonicated emulsions.

correlation between the phenomena occurring in porous media and outside the porous medium allows ua to use coalescence measurement as a screening criterion for many surfactant formulations in predicting their poasible behavior in porous media.

Mobility Control. As mentioned earlier, only a small amount of the microemulsion slug is injected in microemulsion flooding due to the cost of surfactant. Usually a polymer solution is injected after the slug injection. The viscosity of the surfactant slug should be higher than that of oil, and the viscosity of the polymer solution should be higher than that of the aurfactant slug to control the mobility during the oil recovery process. Again due to the economic reason, water or brine is injected after the small amount of polymer solution (usually 0.5 to 1.0 pore volume). The viscosity of the microemulsion can be controlled by choosing a proper alcohol (112). Isopropyl alcohol (113) and tertiary amyl alcohol (114) usually cause a viscosity reduction. A polymer may be added to the microemulsion to increase its viscosity. However, it may cauae a problem, namely, polymer-surfactant incompatibility resulting in the surfactant separation and the high interfacial tension (107, 115, 116). Several researchers (117-120) have diacusaed how to determine oil/water bank mobility in microemulsion flooding.

1.3.4. Effect of Alcohols

In general, a microemulsion formulation for enhanced oil recovery includea a short-chain alcohol as a cosurfactant (112).

The possible effects of such an alcohol include changing viscosity, lowering interfacial tension, reducing interfacial viscosity or changing surfactant partitioning and modifying the solubility of a surfactant in oil or brine phase (107, 112, 121). A previous study (122) auggested that alcohol promotes the masa transfer to the interface and a rapid reduction in the magnitude of the interfacial tension. A mass transfer of an alcohol from the surfactant slug to the oil ganglia in the porous media was shown by Pithapurwala et al. (123).

Iskanderani (124) showed that the separation of an alcohol from a surfactant during the flow through a poroua medium led to poor oil recovery. Even though the change in the composition of the surfactant slug cannot be avoided during the flooding due to the dilution and chromatographic effects of a porous medium, the aeparation of alcohol from surfactant ia minimized at optimal salinity.

Lam (125) did a microvisual study of the residual oil mobilization using a relatively simple chemical system. It was found that under certain circumstances the capillary number required to mobilize the oil drop could be reduced greatly if the displacing phase contained more alcohol than it would in equilibrium with the trapped phase.

1.4 Interaction between Surfactants and Polymers

It has been shown that the solubilization properties of ionic surfactanta in water are changed by addition of nonionic polymers

even if these polymers alone show hardly any aolubilization effect (126-129). Polyvinyl formal (PVF) and polyvinyl butyral (PVB) are insoluble in water and in the usual organic solvents. However, these water-insoluble polymers may be diaaolved in highly concentrated surfactant solution (130). Isemura et al. (131) assumed that polymer molecules are solubilized by oriented adsorption of surfactant molecules in which the nonpolar tail is directed to the polymer and the polar head to the aqueous phase and that the complex would, then, behave like a polyelectrolyte in contrast to the assumption that the nonionic polymer may be solubilized in the micelles. Experimental results from an electron micrograph, viscosity and electrophoretic mobility supported the former assumption (132).

In constraat to the hydrophobic bonding between nonionic polymers and anionic surfactants, Scholtan (133) auggested the ion-dipole interaction between nonionic polymers and anionic surfactants. This was partially supported by Saito (134). He experimentally showed that the ionic group of an anionic surfactant might play a aignificant role in addition to the hydrophobic bonding by the nonpolar parts between the surfactant and the polymer. Further, he ahowed that the oxyethylene group of aurfactants interfered witb the binding of the surfactants to the polymer.

Figure 1-12 shows the surface tension aa a function of the concentration of sodium dodecyl aulfate (SDS) at a fixed concentration of the water-soluble polymer, polyethylene oxide (PEO)

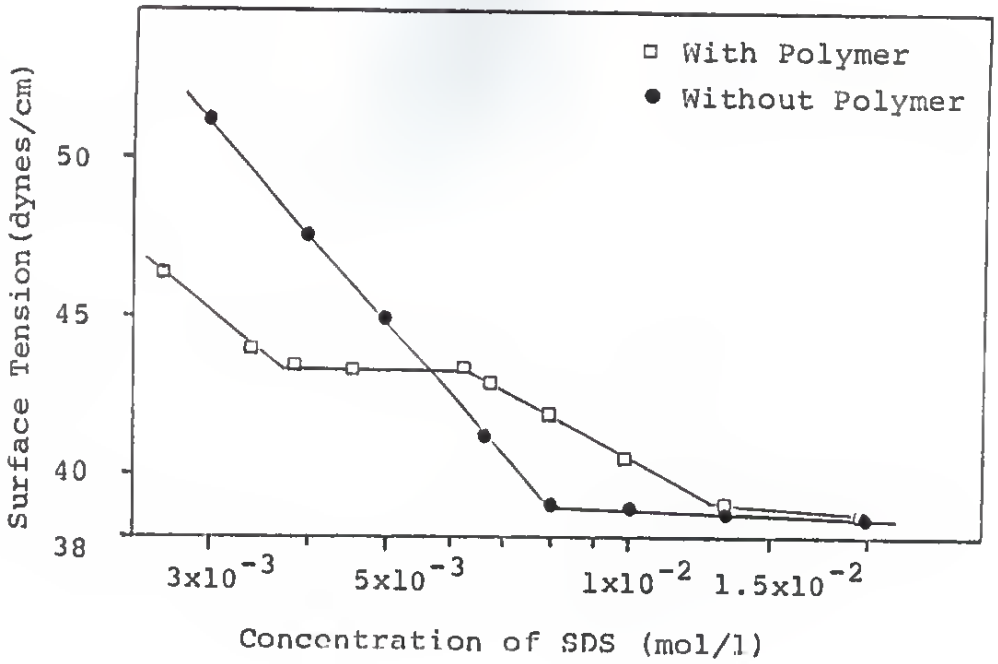


Figure 1-12. Surface tension depending on the concentration of sodium n-dodecyl sulfate (SDS) with and without polymer (polyethylene glycol) (0.02 M).

(135). There are two transitions compsred to only one trsnsition for a surfactsnt solution alone st CMC. Jones (135) interpreted the trsnsition ss follows: 1) Below the first transition, no interaction between the polymer snd surfactant occurred. The surfsce tension snd conductsnce changed in the ssme msnner ss expected in the absence of polymer; 2) st the first trsnsition, surfactants started to be sdsorbed onto the polymer in similsr fashion to micelle formation; 3) between the first and the second trsnsitions, surfsctants were continuously adsorbed onto the polymer until the binding sites were filled; 4) at the second transition, two species are possible, ordinsry SDS micelles and polymer-surfactant complex which differ from those below the second transition.

Saito (136) studied the solubilizstion of aliphatic and aromatic compounds in the surfsctant-polymer complex. He concluded thst solubilizstion depends mainly on the compstibility of the polymer with the solubilizate. He slso concluded that the function of bound surfsctants in solubilization by the complexes was to give the polymers s more hydrophobic chsracter by replacing wster layers around the polymers with surfactsnts and thus to promote contact between the polymers snd the solubilizates. This conclusion is consistent with his esrlier study (137) in the spectroscopic investigation of s dye solubilized in the complex.

Fishmsn snd Eirich (138) did equilibrium dialysis measurements for sn SDS snd poly (N-vinylpyrrolidone) (PVP) system. They suggested that PVP scted as a nuclesting sgent for surfsctant

micelles and stabilized surfactant clusters larger than dimers but smaller than observable in the absence of polymer, that is, the formation of a mixed polymer-surfactant micelle.

It is known that cationic surfactants interact weakly with nonionic polymers (127, 139, 140) while anionic aurfactants interact strongly with such polymers (126-128, 135, 139, 141). While the complex formation with anionic surfactants increased by addition of salts, no complex was formed with cationic surfactants (126, 127). These differences between interactions of cationic and anionic surfactants with nonionic polymers (poly glycol estera) were studied by Schwuger (142). He measured surface tension, conductivity, dye solubilization and the effects of charge on pH of medium. On the basis of these measurements, he concluded as follows: 1) For anionic surfactanta, the interactions between the surfactants and the polymer in water ahould be partly chemical and partly physical in nature. It appears that electrical interaction is significant, too. The oxygen atom of the ether linkage with its lone electron pair could possibly become slightly positively charged, which would favor an adsorption of the negatively charged aurfactant anion. This effect is enhanced by the hydrophobic interaction between the hydrophobic parts of the surfactant and the polymer; 2) for cationic surfactants, there is a repulsion between the positively charged cationic surfactant ion and the ether oxygen atom. In this case, not only ia no electrical attraction operative, but, as a conaequence, there ia a weakening of the hydrophobic bonding between the hydrophobic sections of the two species. His conclusions

essentially agreed with those propoaed for the interaction of SDS with polyvinyl acetate (PVA) (141) and PVP (143).

Smith and Muller (144) studied the chemical shift of the anionic surfactant and nonionic polymer by nmr and dialysis analysia. They showed that the shape of the binding isotherm is not consistent with a Langmuirian binding process. This does not agree with the previous study (136) which showed that the adsorption of surfactant on the polymer molecule could be expressed in terms of the Langmuir adsorption formula.

While there is evidence that cationic polymers do not interact with nonionic surfactants (145, 146), Goddard and Hannan (146) found that cationic polymers interacted with anionic surfactant by the formation of highly surface active polymer-surfactant complex resulting from head to head adsorption of the aurfactant onto the polymer. The observed phenomena were similar to the previous studies for the oppositely charged polymer-aurfactant syatem (147-150): As the concentration of the surfactant increased, turbidity and then precipitation were observed; resolubilization of the precipitate occurred at still greater surfactant concentrations. They also observed the two transitions in the surface tension versus concentration of surfactant aimilar to those represented in Figure 1-12. They explained the first plateau as head-to-head adsorption of the surfactant onto the polymer while the resolubilization at the second plateau occurred by tail to tail adsorption of a second layer of surfactant ions to form a polyanion. Their film balance study

provided evidence of the reaction between polymer and surfactant.

Recently, two different models were proposed to explain the interactions between the polymers and the surfactants by Nagarajan (151) and Ruckenstein et al. (152). In Nagarajan's model, aurfactant aggregatea are adsorbed into the free space of the coiled macromolecules. The latter participates in the formation of aggregates via segments that penetrate the interfacial region of the micelles. In contrast, Ruckenstein'a model does not involve the penetration of the micellar interface by segments of the polymer. Instead, hia model involves the adaorption of micellar aggregates in the free space of the coiled macromolecules.

In summary, most of the studies were done for the nonionic polymer with the anionic or nonionic surfactants and for the oppoaitely charged polymer-aurfactant systems. The different propertiea found in these systems from those in surfactant solution alone were explained by complex formation or the formation of micelles associated with polymer.

Few references are found for similarly charged systems. These systems are reviewed in the later chapter related to the surfactant-polymer interaction between the similarly charged systems.

1.5 Thermal Conductivity of Liquids

Thermal conductivity is a fundamental thermophysical property that is essential for almost all heat transfer application. Reliable thermal conductivity data are needed to interpret many physical and chemical processes as well as to design the equipment

for thermal processes. For example, if the thermal conductivity of the medium with its other properties such as density, viscosity and heat capacity is known, heat transfer rates of a medium flowing through the tubes can be estimated using the dimensionless relationship (153) shown as

$$C_p^{1/3} K^{2/3} \rho^{0.8} \eta^{-0.467} = h_i D_i^{0.2}/0.023 V_i^{0.8} \qquad (1\text{-}5)$$

where C_p = specific heat

K = thermal conductivity

ρ = density

η = viscosity

h_i = heat transfer coefficient

D_i = inside diameter of the tube

V_i = velocity.

The thermal conductivity of a material is the ability of the material to conduct heat and is defined by the Fourier equation (154):

$$q_x/A = - K (dT/dX) \qquad (1\text{-}6)$$

where q_x = heat transfer rate in the x direction

A = area normal to the direction of heat flow

K = thermal conductivity

dT/dx = temperature gradient in the x direction.

Energy transfer by conduction is accomplished in two ways (154). The first mechanism is that of molecular interaction, in which the greater motion of a molecule at a higher energy level imparts energy to adjacent molecules at lower energy levels. This type of transfer is present, to some degree, in all systems in which a temperature gradient exists and in which molecules of a solid, a liquid, or a gas are present. The second mechanism of conduction heat transfer is by free electrons. The free-electron mechanism is significant primarily in pure-metallic solids.

Therefore, the ability of solids to conduct heat varies directly with the concentration of free electrons. Since the mechanism of conduction heat transfer is one of molecular interaction and the molecular behavior of gas, especially dilute gas, is well known, it is relatively easy to develop an equation to estimate thermal conductivity using the result of the kinetic theory of gases with the energy transfer equation (154). In contrast, the thermal conductivity of a liquid as well as a dense gas cannot be easily predicted because the molecular behavior of the liquid phase (as well as the dense gas) is not clearly understood (155). The fact that the mechanism of energy transfer between gas and liquid phases is different can be understood by recognizing the difference between transport-property values in the gas phase and those in the liquid phase: K_l/K_g = 10 to 100, η_l/η_g = 10 to 100, $D_l/D_g = 10^{-4}$ where K_l and K_g are thermal conductivity of liquid and gas respectively, η_l and η_g are viscosity of liquid and gas

respectively, and D_l and D_g are diffusivity of liquid and gas respectively.

In the gaa phase, the molecules are relatively free to move about and transfer momentum and energy by a collision mechanism. The intermolecular force does not drastically affect the values of K, η, or D (156). In a liquid, however, the close proximity of molecules to one another influences strongly the intermolecular forces. Energy and momentum are primarily exchanged by oscillation of molecules in the shared force fields surrounding each molecule (157-159). The use of the information about the intermolecular forces and the structure of the liquid in developing the theory of thermal conductivity of the liquid (160-166) indicates a significant effect of the molecular structure of the liquid on thermal conductivity. Even though a great effort has been made to develop the theory for thermal conductivity of liquids and some progress has been made, a rigorous theory has yet to be proposed.

The prediction of the thermal conductivity of the liquid mixture is even more difficult than the prediction of the thermal conductivity of pure liquids. Even though a number of correlations have been proposed (156, 167-170), only two of them, the Li (168) and power law (156) equationa, can be applied to ternary aystems. In addition, the experimental data for ternary systems are not widely available (171). The local composition model (172) treats deviations from the ideal method (a maas fraction average of the pure component values: $K = \Sigma\ W_i\ K_i$ where W_i is mass fraction of

component i and K_i is pure component thermal conductivity of component i) in terms of deviations of the local composition from random mixing considering binary interactions. However, a recent study (171) showed that further experiments were necessary to check the importance of the ternary interactions because the model performed poorly on some systems. Again, it is expected that the interaction between molecules and the molecular structure of the liquid mixture affect the thermal conductivity of the liquid mixture.

It should be mentioned that the corresponding states techniques for prediction of thermal conductivity have been developed for both liquids (152) and liquid mixtures (172). These methods have a wide range of temperature-pressure applicability, but lack accuracy in predicting composition dependency unless adjustable parameters are used in the mixing rules. In the corresponding states are also implied the effect of the molecular interactions and structure of the liquid or the liquid mixtures on thermal conductivity of the liquid or liquid mixtures.

In summary, thermal conductivity of a liquid depends on the molecular interactions and the molecular structure of the liquid, and that these factors should be taken into account to develop the theory for thermal conductivity of liquids. Because of the complexity and lack of knowledge of the molecular behavior of liquids, theories to date have not led to a simple estimating technique for liquid thermal conductivity (173). Therefore,

approximate or empirical techniques must be used for engineering applicationa (156).

1.6 Phaae Stability of the Gasoline-Methanol Mixture

The uae of alcohol in motor vehicles is not a new technology. An exhaustive international bibliography prepared on the subject can be found before 1920 (174-176). Alcohol fuels have been used in both wartime and peacetime in the United States, and are currently attracting renewed attention as petroleum prices increase and supplies remain uncertain (177). Even though alcohols other than methanol have been considered for blending with gasoline, the current spotlight is on methanol (177, 178). It is known that up to 15% methanol can be added to gasoline in current cars without modification of the engine (178). The addition of methanol to gasoline is advantageous not only in economy but in exhaust quality and performance (179-185). Methanol has an octane rating of 106, compared to typical gasoline ratings of 85 to 100 (186). It prevents knocking and alleviates dieseling when the ignition is switched off. The results for the emiasion tests are not consistent: While Paul (179) reported that both nitrogen oxides (NO_x) and carbon monoxide emissions were decreased considerably with methanol or with gasoline-methanol blends, two other studies (184, 185) reported an overall reduction in carbon monoxide but no consistent and overall change in the NO_x and hydrocarbon emissions. Table 1-1 summarizes the improvement in various performance properties achieved by blending 5 to 30% methanol to 95 to 70% gasoline (187).

Table 1-1. Improved Performance by Blending 5 to 30 Percent Methanol to 95 to 70 Percent Gasoline

Performance	Improvement (%)
Fuel Economy Increase	5-10
CO Emission Decrease	14-72
Exhaust Temperature Decrease	1-9
Acceleration Increase	7

While the gasoline-methanol mixture offers several advantagea, it also has disadvantages compared to gasoline (182): hesitation on warmup, corrosion and phase separation due to lower temperaturea or due to abaorption of water. Among these, phase separation at low temperatures ia found to be most serious problem in practice while the phase separation reaulting from the abaorption of water ia leaa of a problem in practice becauae motor fuela are not freely exposed to the atmosphere (186, 188).

In practice, the chemical atability of fuel in atorage is a function of the structure of its components, together with its purity. With the hydrocarbons, for example, atability ia provided by saturation of the carbon-carbon bonding in the atraight-chain paraffina and in the close-chain naphthenes (above C_5). The alcohola are stable compounds but, as polar moleculea, are active aolvents. The alcohola are, however, less soluble in the non-aromatic (aliphatic) hydrocarbona; therefore ita aolubility in commercial petroleum fuela dependa largely on the hydrocarbon conatituenta of the latter. Solubility alao increasea with temperature. Ethanol and the higher alcohols dissolve more readily in hydrocarbona, and their presence in an alcohol-hydrocarbon blend increasea the solubility of methanol (189, 190). These features are ahown in Figure 1-13 for methanol and for ethanol blended aeparately with keroaene using iao-butanol aa a atabilizer. Aa mentioned earlier, the preaence of even small quantitiea of water in alcohol-hydrocarbon mixturea, however, leada to direct hydrogen bonding between the alcohol and the water

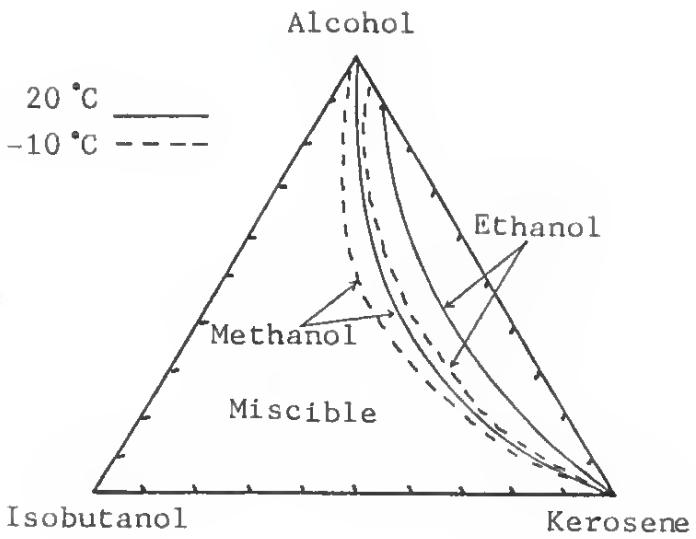


Figure 1-13. Solubility of alcohols in kerosene.

resulting in phase separation, particularly at low temperatures (191). Effect of water on the phase separation of gasoline-alcohol mixture is shown in Figure 1-14. The problem of phase separation at low temperatures due to the small amount of water has been investigated by several researchers (191-196) using various surfactants to form the w/o microemulsions.

In summary, the gasoline-methanol mixture has several advantages compared to gasoline as an automobile fuel. However, the phase separation of the mixture, especially at low temperatures, due to the small amount of water in the mixture presents a serious problem. Even though several researchers showed that the formation of w/o microemulsion using several surfactants was effective in preventing the mixture from phase separation, no systematic study has been done to date.

1.7 Scope

The major goal of this dissertation is to investigate the properties of microemulsions such as solubilization, interfacial tension, thermal conductivity and phase stability as well as the excluded volume effect of polymer in the surfactant solution. The solubilization and interfacial tensions of microemulsions which used nonionic surfactants as cosurfactants in place of short-chain alcohols were examined. Microemulsions prepared by replacing a short-chain alcohol with a proper nonionic surfactant exhibited better properties in relation to solubilization and oil displacement in porous media. Thermal conductivity studies of microemulsions

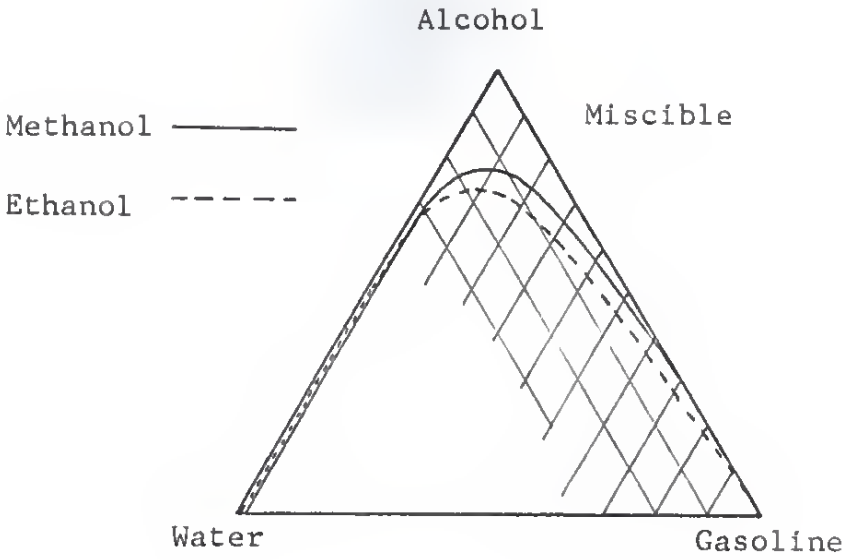


Figure 1-14. Solubility of alcohols in gasoline in the presence of alcohol.

indicated the effect of microatructure on thermal conductivity. The possible use of the microemulsions as lubricant oil, heat transfer fluid, etc. is discussed. The phase stability of the methanol-isooctane-toluene mixture was studied at -25 °C using alcohols and/or surfactants to determine the structural effect of the additive(s). The results are relevant to the the development of alternative fuels. The mechanism of the decrease of interfacial tension of polymer solution by the addition of a small amount of a surfactant was investigated using static and dynamic light scattering techniques.

Following the brief review of microemulsions, enhanced oil recovery and thermal properties of liquids, Chapter 2 reports the relationship between the solubilities of water in alcohol-free w/o microemulsions and the efficiency of the oil displacement by the microemulsions. Further, the displacement mechanism for the alcohol-free w/o microemulsions is proposed which was in qualitative agreement with the oil displacement experiments. In Chapter 3, the advantages of using a nonionic surfactant as a cosurfactant instead of short-chain alcohols for the displacement of heavy oils are dicussed.

Chapter 4 focuses on the effect of polymer molecules on surfactant aolutions. The results indicate that the mecbanism of decrease in interfacial tension of anionic polymer solutions upon addition of a small amount of anionic surfactants is much different from that of nonionic polymer-ionic surfactant solutions. The

excluded volume of polymer was obtained by light scattering experiment to support the proposed mechanism.

Chapter 5 experimentally demonstrates the effect of the microstructure of a liquid on thermal diffusivity using two liquids having much different microstructures. As an extension, thermal conductivities of microemulsions are measured and are compared with predicted values using existing equations for liquid mixtures. A simple transient method to measure the thermal diffusivity of a liquid is developed for the study and is described.

Chapter 6 reports the effect of surfactants and/or alcohols on the phase stability of a methanol-isooctane-toluene mixture at -25 °C and further delineates how the molecular structures of various surfactant and/or alcohols influence the phase stability of the mixture at -25 °C. The possibility of the formation of a waterless microemulsion is discussed.

Finally, Chapter 7 summarizes the conclusions from the entire study and provides recommendations for future research in areas related to this dissertation.

CHAPTER 2

ALCOHOL-FREE WATER-IN-OIL MICROEMULSIONS

2.1 Introduction

Microemulsions for enhanced oil recovery have received much attention because of their ability to lower the interfacial tension between residual oil and reservoir water (or brine), resulting in enhanced oil recovery. All three microemulsion structures, namely, the lower-, middle-, and upper-phase microemulsions, have been studied for enhanced oil recovery (76-78, 93, 101, 102, 104, 109, 114, 197-204). The lower- and upper-phase microemulsions are o/w- and w/o microemulsions, respectively, while several microstructures of the middle phase microemulsions have been proposed. Scriven (50) proposed that the middle-phase microemulsion may have a bicontinuous structure of oil and water with intervening surfactant layers. Shah et al. (205) and Miller et al. (73) believe that the middle phase microemulsion may be coacervated droplets. Sinoda and Friberg (13) proposed that the middle-phase microemulsion is an essentially lamellar structure with alternating layers of oil and brine. The effect of the structures of the lower- and the upper-phase microemulsions on the oil recovery is not clearly understood due to difficulty in conducting experiments because a change in the structure of the microemulsion always accompanies changes in other

parameters such as the concentrations of the components, viscosity, interfacial tension, and so on (206). However, regardless of their structural differences, these microemulsions commonly employ short-chain alcohols as cosurfactants (112). While a short-chain alcohol is necessary to form the microemulsion by increasing the fluidity of the interface, it has less solubilization capacity than a surfactant (102). Even though short-chain alcohols as a cosurfactant in a microemulsion are successful for light oil recovery, they are less effective for heavy oil recovery due to poor solubilization capacity of heavy-oil microemulsions. The interfacial tension of the microemulsion with excess oil or brine is high due to the small solubilization of heavy oil in the microemulsion containing a short-chain alcohol. It is known that the solubilization of brine in a w/o microemulsions decreases as the chain length of oil increases at corresponding optimal salinity (207).

An alcohol-free w/o microemulsion was formulated by replacing a short-chain alcohol with a nonionic surfactant. By using a nonionic surfactant instead of a short-chain alcohol, the solubilization of brine in heavy oil containing microemulsion increased. After testing several nonionic surfactants with sn snionic surfactant, Aerosol-OT (AOT), it was found that the system consisting of AOT and Arlacel 20 was best for solubilizing water in the heavy oil microemulsion. The formulated alcohol-free w/o microemulsion showed that its solubility of water depended on the weight ratio of the two surfactants which, in turn, influenced oil recovery. The oil

displacement mechanisms by the w/o microemulsions which were proposed were qualitatively supported by oil displacement experiments. In addition, the effects of concentration of the electrolytes and that of surfactants on the oil recovery by the w/o microemulsion were studied.

2.2 Materials and Methods

2.2.1 Materials

Mineral oil supplied by Witco Chemical Corporation was used to simulate a heavy oil. Specific gravity and viscosity of the mineral oil were 29.2 API and 240 cP at 60 ^{o}F (160 cP at room temperature), respectively. An anionic surfactant, AOT (sodium dioctyl sulfosuccinate), was purchased from American Cyanamid and a nonionic surfactant, Arlacel 20 (sorbitan monolaurate), was a gift from ICI Americas, Inc. Their chemical structures are shown in Figure 2-1. De-ionized, distilled water was used in all experiments. Brine was prepared by adding NaCl into de-ionized, distilled water. Sodium chloride was purchased from Fisher Scientific Company and was of certified grade. The oil-soluble dye, Sudan III was purchased from Eastman Kodak Corporation and the polymer Pusher 700 (polycrcylamide) was purchased from Dow Chemical Company. All chemicals were used as received without further purification.

Unconsolidated sand packs were used for oil recovery experiments. Figure 2-2 schematically shows the experimental set-up for the oil displacement experiments. Each sand pack was prepared

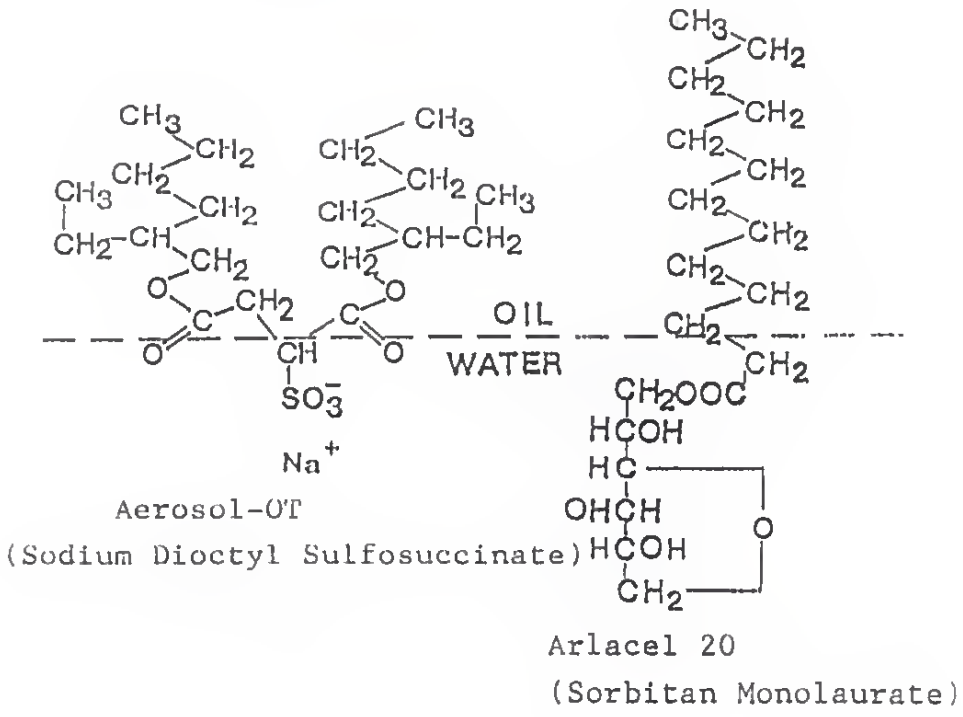


Figure 2-1. Structures of aerosol-OT and arlacel 20.

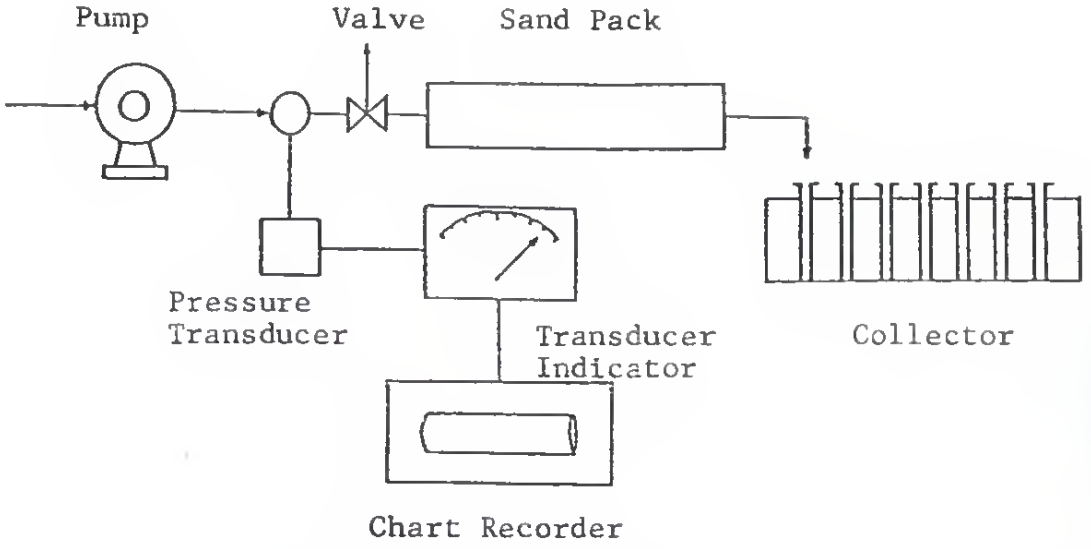


Figure 2-2. A schematic diagram of the experimental set-up for oil displacement studies.

by filling a cylindrical glass tube with sand while continuously shaking and tapping the tube. The dimension of a sand pack was 0.95 inch in diameter and 2 feet in length. The average porosity of a sand pack was 0.39. Each sand pack was used for a single experiment.

2.2.2 Methods

Solubility of Water. To measure the maximum solubility of water, the alcohol-free water-in-oil microemulsion was prepared by first dissolving the surfactants into mineral oil. The resulting solutions contained 0.4g surfactants/ml mineral oil and the weight ratios of AOT to Arlacel 20 varied from 0 to 3. These solutions were titrated with water at room temperature (25 ^{o}C ± 1 ^{o}C). Water was added drop-by-drop into the oil-AOT-Arlacel 20 solution and the solution was stirred. After each addition of water, the solution was checked for clarity and then for birefringence using polarizing plates. The amount of water required to make the solution turbid and/or birefringent was considered the end point for maximum solubilization.

Phase Behavior. Phase behavior was studied at the weight ratio, 13:27, of AOT to Arlacel 20 at which the solubility of water in the microemulsion was maximum. Nine samples having different weight ratios of surfactants to mineral oil were first prepared and then water was added. The amount of water in each addition was 0.1 ml. After each addition, the samples were placed in a constant

temperature container ($30^{o}C$) for 3 days and were then checked to see whether these showed one or two phases. In the study of phase behavior, an oil soluble dye was added into mineral oil to check the continuous phase of the microemulsion.

Viscosity. Viscosity of the microemulsions was measured as a function of water content using a Brookfield LVT type viscometer at shear rate of 5.75 sec^{-1}.

Electrical Resistance. Electrical resistance of the alcohol-free w/o microemulsions was measured as a function of water content using electrodes connected to Beckman Conductivity Bridge Model RC 16B2. Two glass-sealed silver wires (diameter = 0.16 cm) were used as electrodes. A one cemtimeter length at the end of each wire was exposed outside the glass tube, and the Ag-AgCl electrodes were separated by 0.8 cm. The electrodes were electro plated in dilute HCl to produce Ag-Cl electrodes. The electrical resistance of the microemulsions was measured by dipping the electrodes into the microemulsions.

Oil Recovery. The entrapped air in a sand pack was displaced by the flow of carbon dioxide. Then the pore volume of a sand pack was measured by flowing water. Next, oil was pumped in until no water came out. Saturated oil was then displaced by water until the production ratio of oil to water was less than 0.01. Residual oil

after water flooding was displaced by the 0.1 pore volume of the microemulsion followed by the half pore volumes of a polymer aqueous solution followed by water injection until no oil came out. During oil recovery experiments, the flow rates of fluids were 1 ft/day except during the initial water and oil saturation. To test the effect of salt on the oil recovery, brine (2.6% NaCl, w/v) was used except for tertiary oil recovery in which only de-ionized, distilled water was used.

2.3 Solubility of Water in the Alcohol-Free Water-in-Oil Microemulsions

The combination of Arlacel 20 and AOT was chosen from the several combinations of nonionic and anionic surfactants because this combination had been found to be the best system for the solubilization of water in the w/o microemulsions in a previous study (208). The solubility of brine in the w/o microemulsion should be large enough to produce the low interfacial tension between water and the microemulsion. The previous study had also shown that the amount of water solubilized in the alcohol-free w/o microemulsion depended on the weight ratio of these two chosen surfactants and the kind of oil used. It was shown that the interfacial tension depended on the solubility of water in the w/o microemulsion. Therefore the solubility of water in the w/o microemulsion was first investigated using the mineral oil.

The results are shown in Table 2-1 and Figure 2-3. For mineral oil, the maximum solubility of water was obtained at the weight

Table 2-1. Solubility of Water in the Alcohol-Free W/O Microemulsion[c]

Ratio of Surfactants by Weight	AOT[a]	0	10	11	13	14	15	20	25	30
	A20[b]	40	30	29	27	26	25	20	15	10
Maximum Water to Oil Ratio by Volume		0.04	0.23	0.28	0.83	0.81	0.76	0.54	0.22	0.06

a. AOT means an anionic surfactant, Aerosol-OT.

b. A20 means a nonionic surfactant, Arlacel 20.

c. The system consisted of 4 g of total surfactant in 10 ml of mineral oil as the initial solution. The water was added to this solution untiil it became turbid.

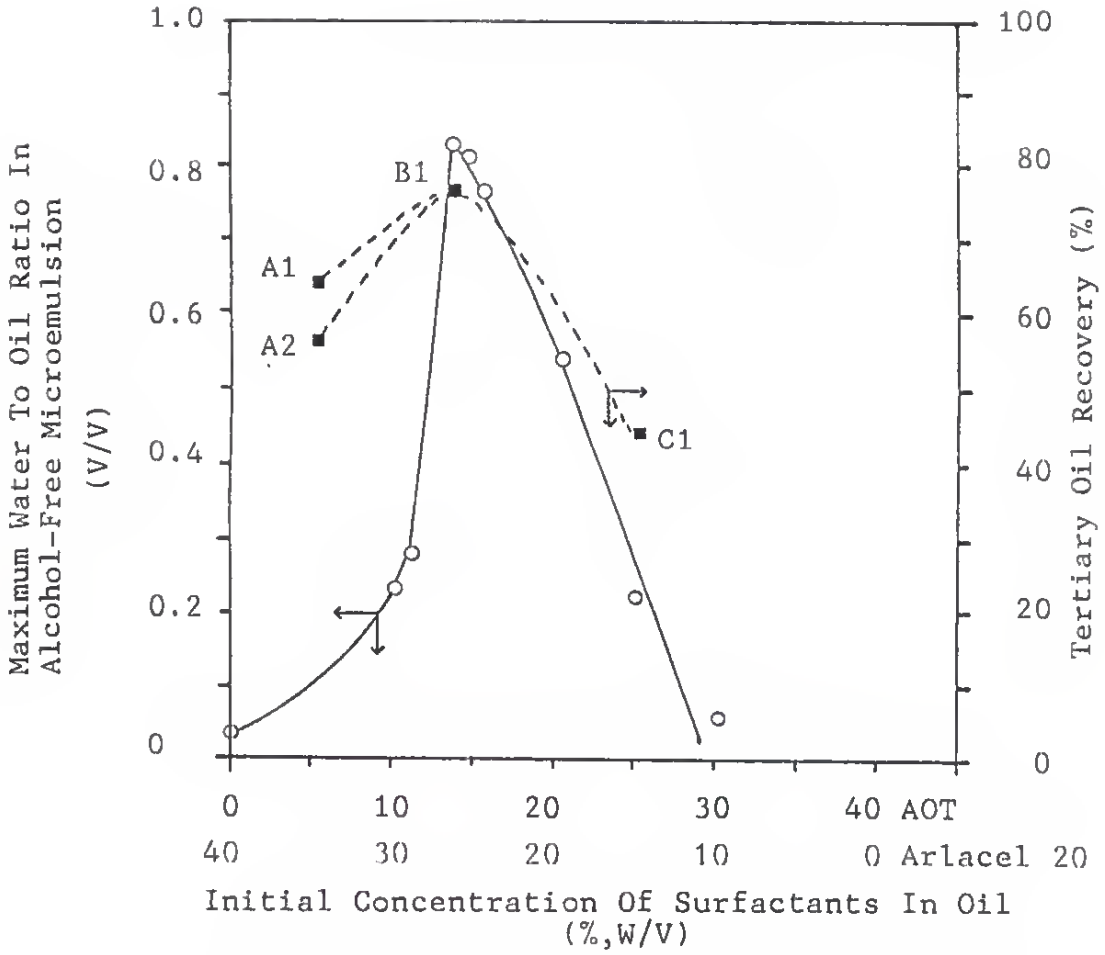


Figure 2-3. Solubility of water in the water-in-oil microemulsion, Compositions of the slugs A1, A2, B1 and C1 are represented in Table 2-3.

ratio, 13:27, of AOT to Arlacel 20 and the volume ratio of water to oil was 0.83. It had been shown that the ratio of surfactants for the maximum solubility of water had been shifted towards more Arlacel 20 as the chain length of oil increases (208). Therefore the weight ratio of the surfactants for mineral oil was reasonable compared to the weight ratio, 20:20, for hexadecane in the previous study (208). It should be noted that the solubility sharply decreased in both directions from the ratio having the maximum solubility. In other words, the capability of the w/o microemulsion to accommodate water can be dramatically changed by a small change in the composition of the chosen surfactants. This fact emphasizes the necessity of selecting a proper combination and composition of surfactants for the high water solubilization in the w/o microemulsion, because solubility is related to the efficiency of oil recovery as shown in Figure 2-3: the oil recovery was maximum (76.2%) when the solubilization of water in the w/o microemulsion was largest.

2.4 Phase Behavior of the Water-In-Oil Microemulsions

Figure 2-4 shows the pseudo-ternary diagram. One phase region was large and appeared to be oil continuous microemulsion determined as follows. The oil soluble dye, Sudan III was added to the microemulsion. The dye quickly dissolved in the external oil phase of the microemulsion. In contrast, in the water-external system, the uptake of the dye was very slow or none at all. This was supported by measurements of viscosity and electrical resistance as

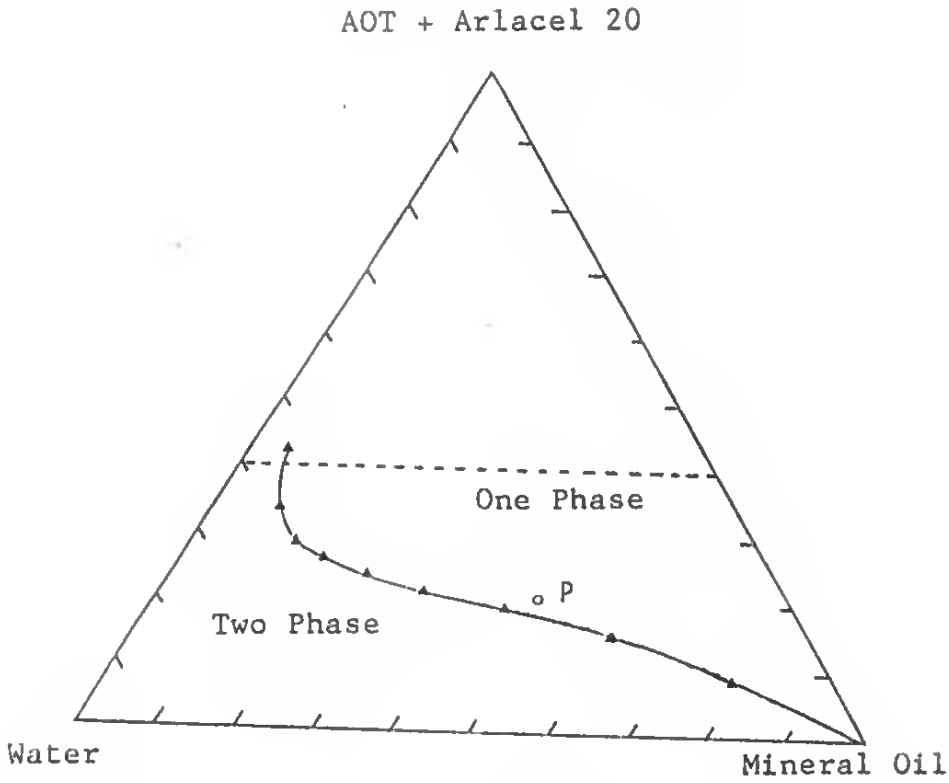


Figure 2-4. Phase diagram. P represents the typical composition of the water-in-oil microemulsion slug.

a function of the amount of water in the microemulsion. Figure 2-5 shows the results of viscosity measurements. As the amount of water in the microemulsion increased, viscosity also increased. If phase inversion from oil to water phases had occurred, there should have been an abrupt change in viscosity (209, 210). As represented in Table 2-2, the values of electrical resistance were greater than 7.8 x 10^5 ohms, indicating oil continuous phase in the microemulsion (210). Up to the ratio, 0.6, of water to oil, electrical resistances were out of range indicating that their electrical resistances were greater than 2.5 x 10^6 ohms. Based on the results from three independent techniques, namely, dye solubilization, viscosity and electrical resistance measurements, it was concluded that the microemulsions formed were oil-external.

2.5 Proposed Mechanism of Oil Displacement by Water-in-Oil Microemulsions

The slug can be of any composition in the one phase region around the boundary line in Figure 2-4. The region above the broken line was not of interest due to the economic considerations. Typical composition (P) of the slug is shown in Figure 2-4. In Figure 2-6, (a) shows the relative volumes of water and oil in the porous medium just after the secondary oil recovery by water, while (b) shows that after slug injection. After injection of the slug, two phases are formed, namely, oil-external microemulsions and excess water. Since the w/o microemulsion is oil continuous, it can be miscible with residual oil while it is immiscible with residual

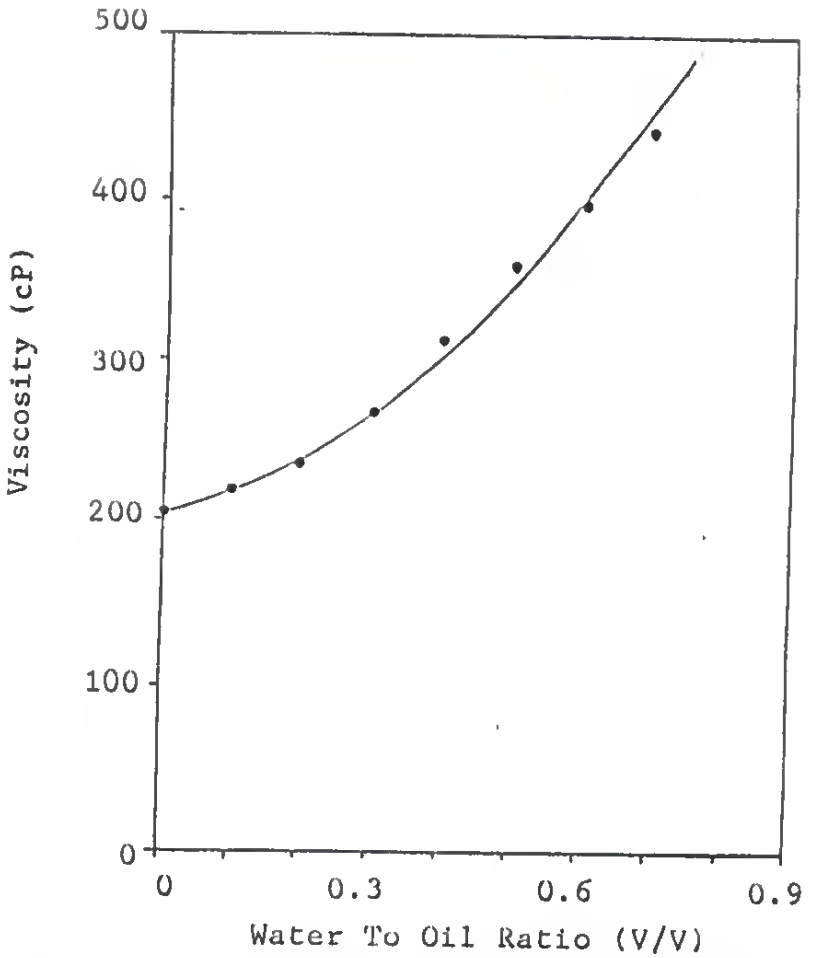


Figure 2-5. Viscosity of the water-in-oil microemulsion as a function of the amount of water added to the oil plus surfactants mixture. Surfactant ratio = aersol-OT/arlacel 20 = 13/27 (w/w).

Table 2-2. Electrical Resistance of the Microemulsions Depending on the Amount of Water in the Microemulsions

Ratio of Water to Oil by Volume	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Resistance (ohms)	Greater than 2.5×10^6							9.0×10^5	7.8×10^5

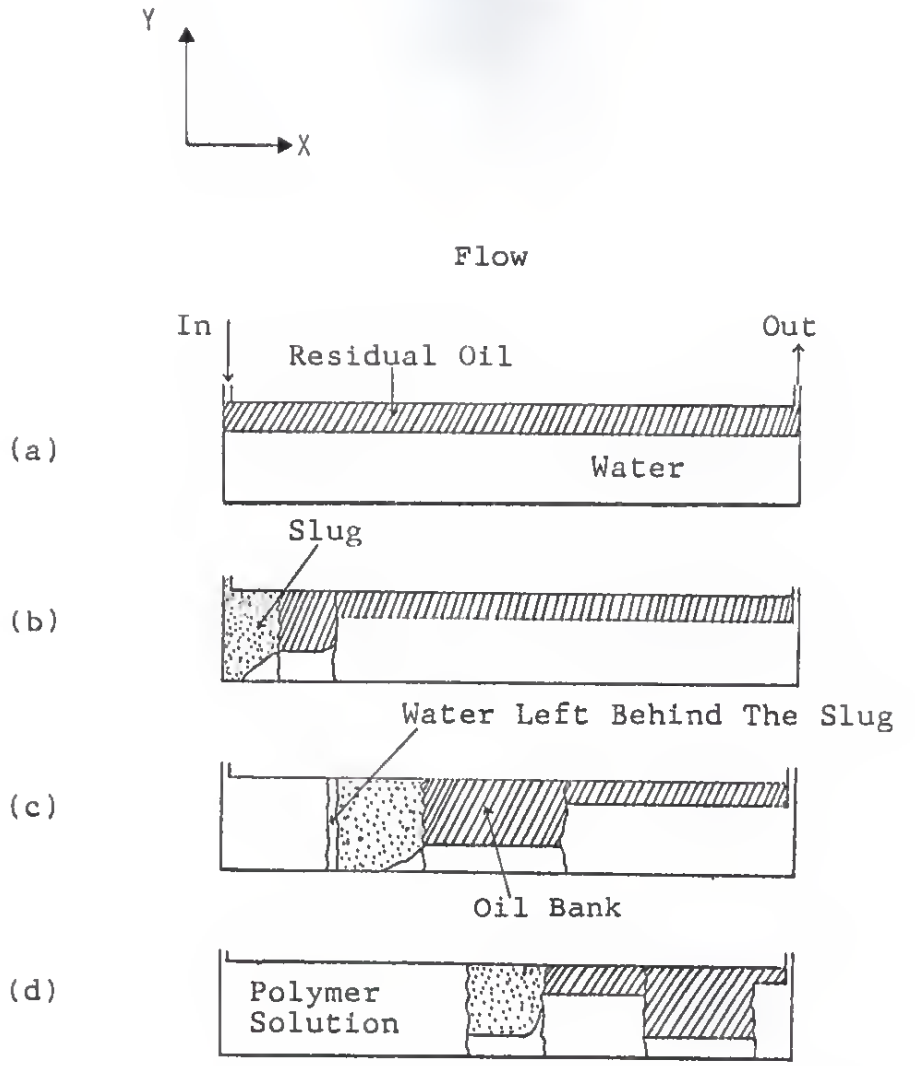


Figure 2-6. A schematic presentation of the relative volume of oil and water in a porous medium during oil displacement by the water-in-oil microemulsions. (a) after water flooding; (b) surfactant slug injection; (c) oil bank formation; (d) the injection of polymer solution. X-axis represents the distance along the porous medium and Y-axis represents the relative volumes of oil and water.

water. Therefore the residual oil contacted by the slug is miscibly displaced and starts to form the oil bank. Most of reaidual water is displaced immiscibly by the alug, but some is carried by the front part of the slug in the form of w/o macroemulsion (211), while a fraction of water and a fraction of the slug are left behind, depending on the interfacial tension produced by the w/o microemulsion as shown in (c). Then, the water left behind the slug is miscibly displaced by polymer solution and starts to form a water bank. If this water bank takes over the front part of the slug, then the fractional flow of oil in the stabilized oil bank is reduced as shown in (d). Further, if the water bank takes over even the front part of oil bank, the high fractional flow of oil bank (or oil cut) cannot be obtained, resulting in poor oil recovery. This will result in the leaky-piston mechanism (d) of displacement (211). However, if the w/o microemulsion can produce a aufficiently low interfacial tension, the amounts of water left behind the alug can be reduced and the formation of water bank is delayed, resulting in good oil recovery. In this case, the mechanism of displacement is more piston-like (c).

2.6 Experimental Results of Oil Displacements

Oil recovery experimenta were designed to elucidate the effects of the following variables: 1) effect of compositions of the w/o microemulsions, 2) effect of the amount of water in the w/o microemulsions, 3) effects of polymer flooding, 4) effect of oil as

the slug, and 5) effects of the concentration of salt and aurfactant in the slug on tertiary oil recovery.

2.6.1 Effect of the Composition of the W/O Microemulsions on Oil Displacement

Four different compositions of the microemulsions shown as A1,B1,C1, and A2 in Figure 2-3 and Table 2-3 were used as the microemulsion slugs for tertiary oil recovery. Now consider three microemulsion slugs, A1, B1, and C1. Each w/o microemulsion slug contained 80% of its maximum solubility of water. Figure 2-3 and Table 2-3 show the experimental results. Tertiary oil recovery was the best for composition B1. This was expected because the better solubilization capacity of water in the w/o microemulsion would result in lower interfacial tension at microemulsion/water or polymer solution interface which, in turn, resulted in the better efficiency of oil recovery. These experimental results can be viewed in another way by investigating the production histories as shown in Figure 2-7. Every curve consists of three linear parts with different slopea. The first linear part with the lower slope up to 0.4 pore volumes of injected fluids was due to the formation of oil bank and the second linear part with the higher slope was due to the flow of the stabilized oil bank. The final linear part with the zero slope was due to surfactant breakthrough. Since the residual oil was viscoua, the fractional flow of oil in the stabilized oil bank (called oil cut) was high as shown in Figure 2-8. The values of oil cut in the stabilized oil bank were almost same for the three

Table 2-3. Effect of Composition of the Microemulsion Slugs on Oil Displacement Efficiency

Slug Symbol		A1	B1	C1	A2
Composition of Surfactant Slug	Mineral Oil	10 ml	10 ml	10 ml	10ml
	AOT[a]	0.5 g	1.3 g	2.5 g	0.5 g
	A20[b]	3.5 g	2.7 g	1.5 g	3.5 g
	Water	0.8 ml	6.64 ml	1.76 ml	0.8 ml
Volume % of Surfactants in microemulsion Slug		23.9	17.0	24.6	23.9
WOR_{max}[c]		0.1	0.83	0.22	0.1
Size of Slug injected		0.1	0.1	0.1	0.076
Pore Volume of Sand Pack (PV)		111 ml	105 ml	103 ml	104 ml
Porosity of Sand Pack		0.405	0.383	0.376	0.379
Oil Saturation (% PV)		82.0	88.6	85.4	88.5
Secondary Oil Oil Recovery[d] (%)		46.2	43.0	50.0	47.8
Residual Oil[d](%)		53.8	57.0	50.0	52.2
Tertiary Oil Recovery[e] (%)		64.1	76.2	43.1	56.4
Total Oil Recovery[d] (%)		79.3	85.8	69.6	76.1
Emulsion or Surfactant Break-through (PV)		0.68	0.81	0.57	0.66

a. AOT means an anionic surfactant, Aerosol-OT.

b. A20 means a nonionic surfactant, Arlacel 20.

c. is the maximum water to oil ratio by volume in the microemulsion.

d. Calculated based on the saturated oil.

e. Calculated based on the residual oil.

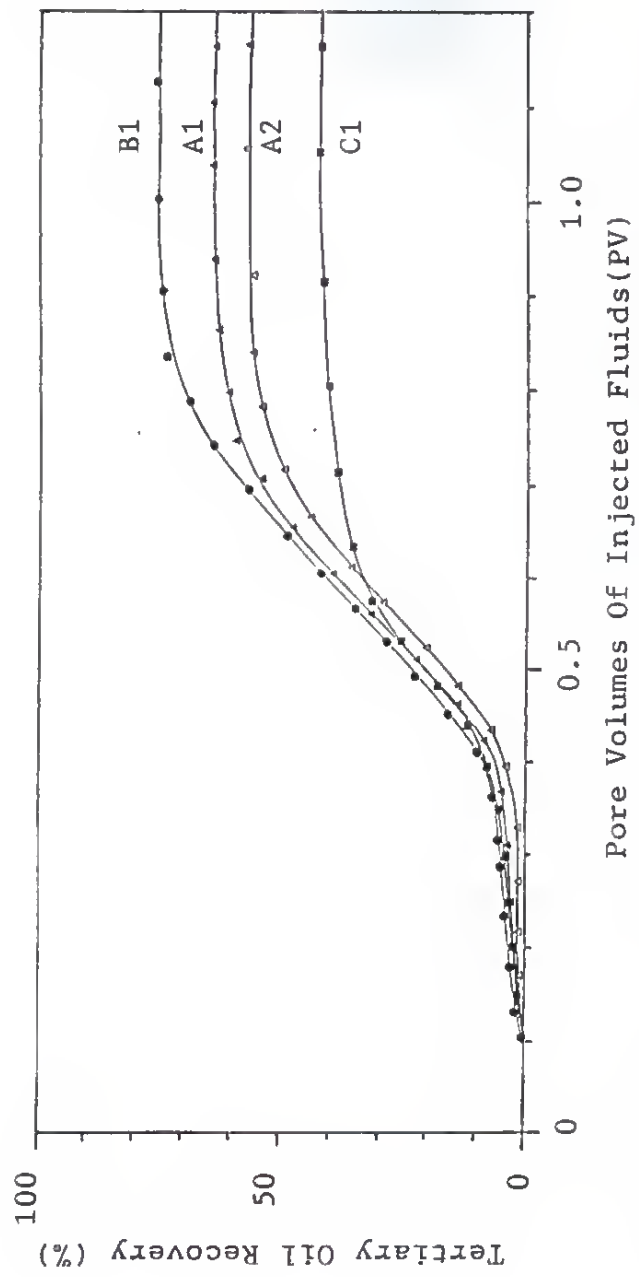


Figure 2-7. Effect of composition of the water-in-oil microemulsion on oil displacement efficiency. The compositions of the microemulsion slugs A1, A2, B1 and C1 are represented in Table 2-3.

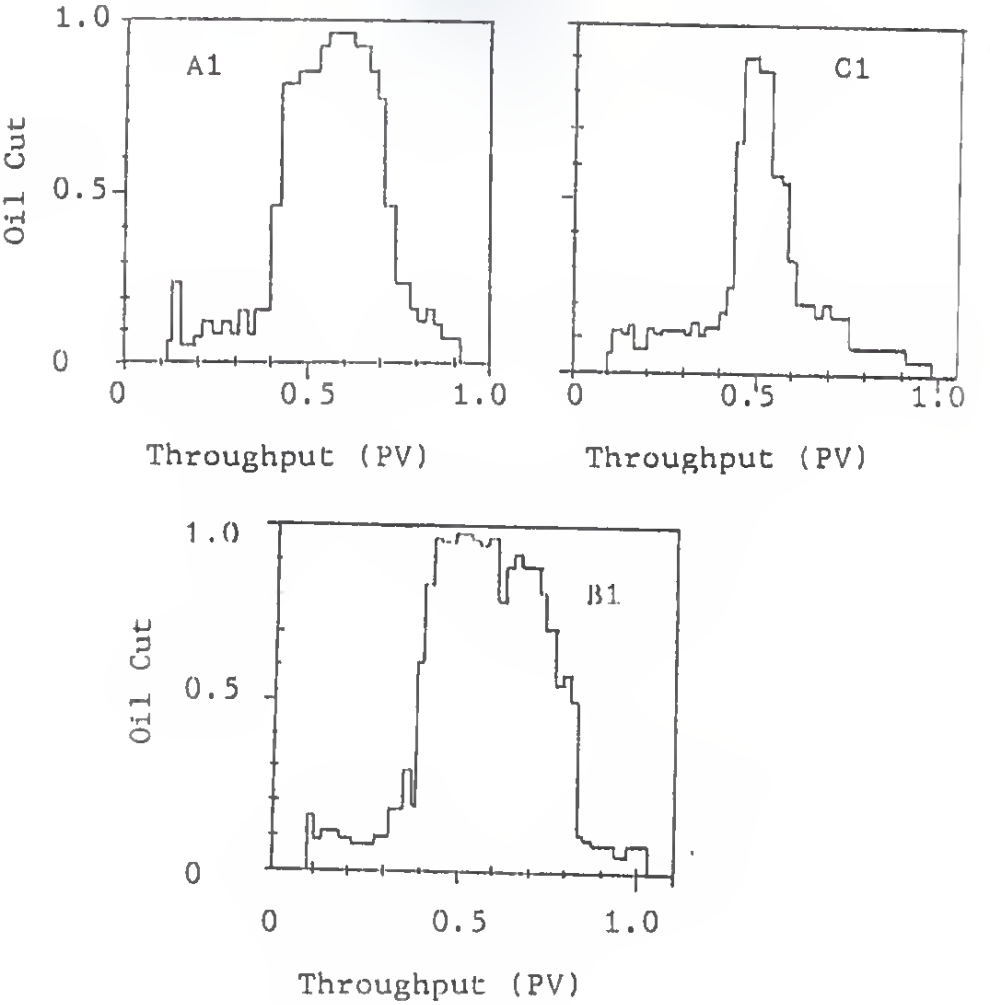


Figure 2-8. Oil production histogram. The compositions of the microemulsion slugs A1, B1 and C1 are represented in Table 2-3.

different microemulsion slugs; thus the second linear part of every curve has nearly the same slope as seen in Figure 2-7. Figure 2-8 shows that, for the microemulsion alug C1, the water bank was formed and took over the microemulaion alug at the early stage of tertiary oil recovery, resulting in poor oil recovery with a lower oil cut. A previous study (211) showed that the emulsion breakthrough became faster as the amount of water which could not be displaced by the slug increased. As shown in Table 2-3, Emulsion breakthrough was slowest for B1. Table 2-3, Figure 2-7, and Figure 2-8 show that the efficiency of oil recovery leveled off after the emulaion came out. It should be noted that the microemulsion slugs A1 and C1 contained more surfactants than the microemulsion slug B1 because, while the sizes of the slugs were same for all three (0.1 pore volume), the amounts of water in the slugs A1 and C1 were much less than that in the slug B1.

The microemulsion slug, A2, in Table 2-3, and Figure 2-7 had the same composition as the microemulsion slug A1 but the size of the slug was reduced from 0.1 to 0.076 pore volumes so that the amount of surfactants in the slug A2 was the same as that in the microemulsion slug B1. This further decreased the efficiency of tertiary oil recovery from 76.2 to 56.4% as shown in Table 2-3 and Figure 2-7. This suggests that the ratio of surfactanta, and hence the solubilization capacity is more important than the total amount of the surfactants. Figure 2-8 also shows how much faster the water bank took over slug C1 than slug B1.

Now, let's try to qualitatively prove the proposed mechanism by using the experimental data. Consider the typical cases, slugs B1 and C1. The microemulsion at the composition B1 had the best capability to accommodate water while the microemulsion at the composition C1 had the small solubilization of water. Therefore, B1 produced the lowest interfacial tension while C1 produced the high interfacial tension against excess water phase. If our proposed mechanism is correct, the formation of water bank for the slug C1 should occur earlier than that for the slug B1 because of the larger amount of water left behind the slug C1 due to higher interfacial tension of the microemulsion against the residusl water at C1. Indeed, as shown in Figure 2-8, the formation of the water bank occurred at about 0.8 pore volumes of the throughput for the slug B1 while it occurred at about 0.55 pore volume of the throughput for the slug C1. Therefore, the lower interfscial tension produced by the slug B1 resulted in the good oil recovery by the more piston-like displacement while the higher interfacial tension of slug C1 resulted in the poor oil recovery by the leaky piston displacement.

2.6.2 Effect of the Amount of Water in the W/O Microemulsions on the Oil Displacement

Additional experiments were performed using the compositions B2 and B3 as the microemulsion slugs represented in Table 2-4. The sizes of the slugs were sdjusted so that the amounts of the surfactants in slugs B2 and B3 were the same as that in the slug B1. The sizes of slugs B2 and B3 were 0.087 and 0.067 pore volumes,

Table 2-4. Effect of the Amount of Water in the W/O Microemulsion Slugs with the Same Composition on Oil Displacement

Slug Symbol		B1	B2	B3
Composition of Surfactant Slug	Mineral Oil	10ml	10 ml	10 ml
	AOT[a]	1.3 g	1.3 g	1.3 g
	A20[b]	2.7 g	2.7 g	2.7 g
	Water	6.4 ml	4.00 ml	0.00 ml
WOR_{max}[c]		0.83	0.83	0.83
Total Amount of Surfactant in the Slug		2.1 g	2.1 g	2.1 g
Size of Slug (PV)		0.100	0.087	0.067
Vol. % of Surfactants in Slug		17.0	18.9	25.5
Pore Volume of Sand Pack (PV)		105 ml	104 ml	103 ml
Porosity of Sand Pack		0.383	0.379	0.376
Oil Saturation (% PV)		88.6	84.6	85.4
Secondary Oil Recovery[d] (%)		43.0	47.7	47.7
Residual Oil[d](%)		57.0	52.3	52.3
Tertiary Oil Recovery[e] (%)		76.2	69.3	67.3
Total Oil Recovery[d] (%)		85.8	83.1	82.0
Emulsion or Surfactant Break-through (PV)		0.81	0.80	0.79

a. AOT means an anionic surfactant, Aerosol-OT.

b. A20 means a nonionic surfactant, Arlacel 20.

c. is the maximum water to oil ratio by volume in the microemulsion.

d. calculated based on the saturated oil.

e. calculated based on the residual oil.

respectively. The effect of the initial amount of water in the w/o microemulsion on the oil recovery had a small effect on oil displacement efficiency as shown in Figure 2-9 and Figure 2-10. The small difference in the efficiency of oil recovery seemed to be caused by the different sizes of the slugs because the smaller size of the slug resulted in a little earlier formation of the water bank even though the effect was not significant in this case.

2.6.3 Effect of Polymer Flooding and Oil as a Slug on the Oil Displacement

To evaluate the better efficiency of oil recovery by the w/o microemulsion flooding than that of polymer flooding, a half pore volume of polymer solution was injected right after the water flooding (polymer flooding). The results are shown in Table 2-5, Figure 2-11, and Figure 2-12. The recovered oil represented about 48.8% which was comparable to the efficiency of the slug C1 (43.1% as represented in Table 2-3). This again indicates that the slug C1 did not have an interfacial tension low enough to displace much of water and hence permitted the early formation of the water bank which eventually took over the slug and the oil bank. However when the slug exhibited a low interfacial tension as is the case for B1, it could recover an 27 percent more oil than the polymer flooding by displacing much of water and delaying the formation of the water bank.

Since the w/o microemulsion had an advantage of forming an oil bank due to its compatibility with the residual oil, it was

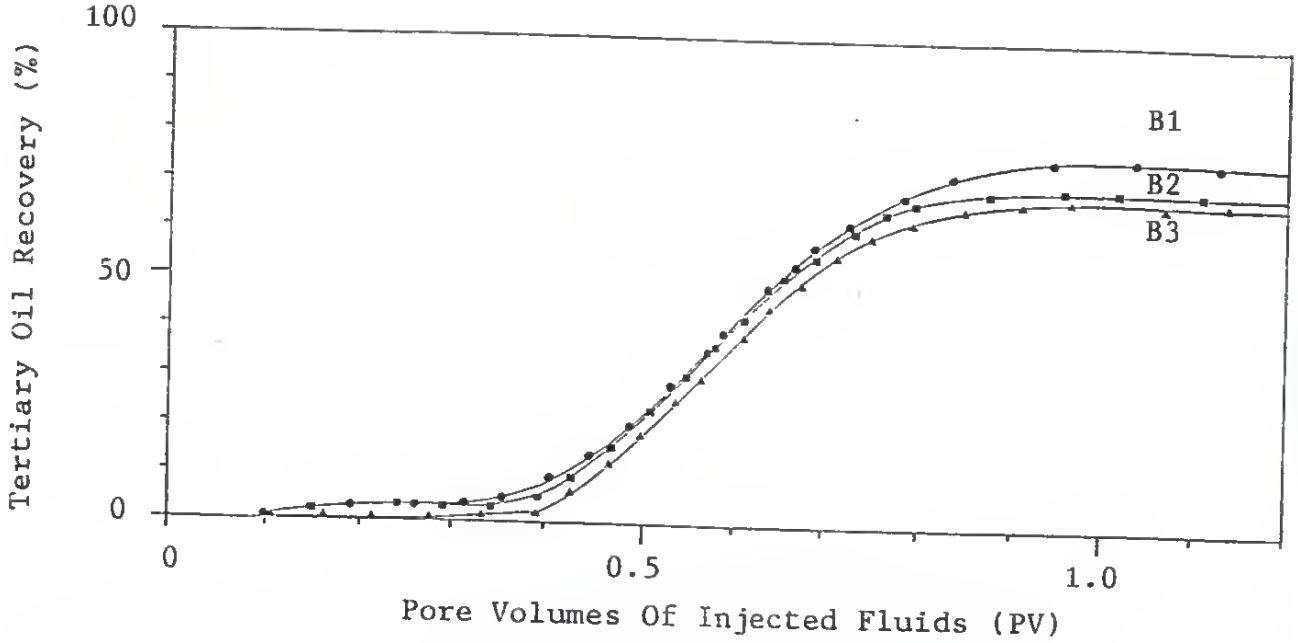


Figure 2-9. Effect of water in the water-in-oil microemulsion on oil displacement efficiency. The compositions of the microemulsion slugs B1, B2 and B3 are represented in Table 2-4.

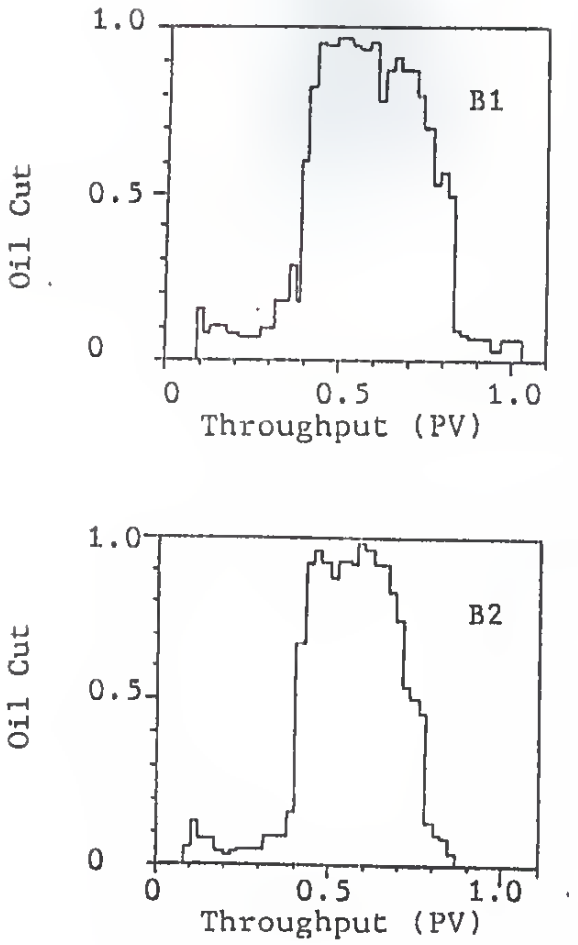


Figure 2-10. Oil production histogram. The compositions of the microemulsion slugs B1 and B2 are represented in Table 2-4.

Table 2-5. Effect of Polymer Flooding and Oil as Slug on Oil Displacement

	Polymer Flooding	Mineral Oil as the Slug	Micro-emulsion
Pore volume of Sand Pack(PV)	100 ml	105 ml	105 ml
Porosity of Sand Pack	0.365	0.383	0.383
Oil Saturation (% PV)	91.0	85.7	88.6
Secondary Oil Recovery[a](%)	49.5	52.2	43.0
Residual Oil[a](%)	50.5	47.8	57.0
Tertiary Oil Recovery[b](%)	48.8	52.5[c]	76.2[c]
Total Oil Recovery[a](%)	74.1	74.7	85.8

a. Calculated based on the saturated oil.

b. Calculated based on the residual oil.

c. Size of oil as the slug was 0.1 PV and this was taken into account for calculation of oil recovery.

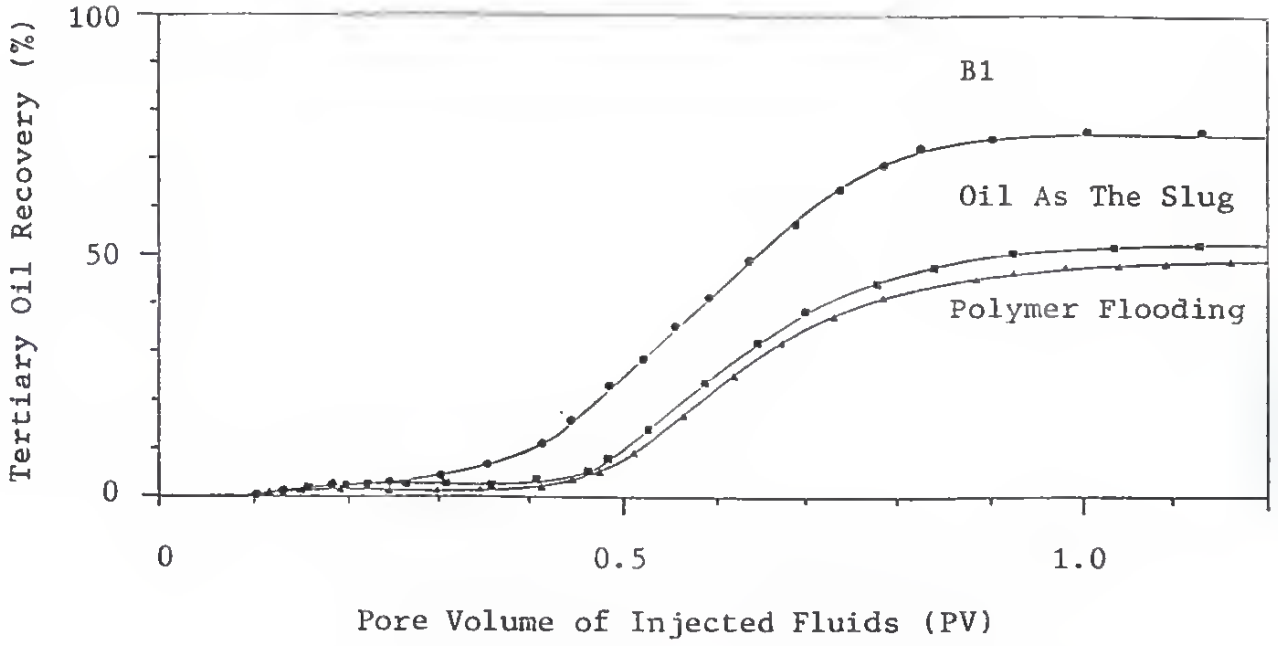
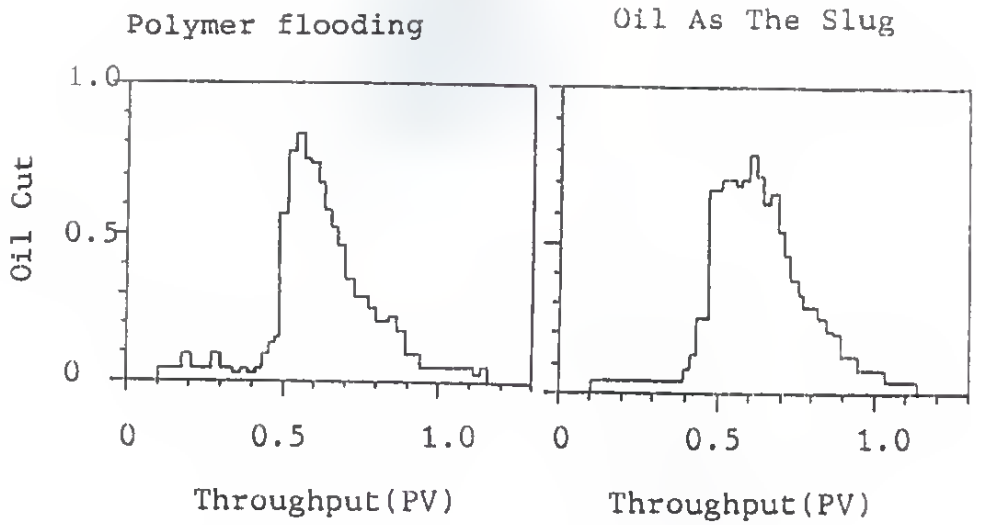


Figure 2-11. Effect of polymer flooding and oil as the slug on oil displacement efficiency. The composition of the slug B1 is represented in Table 2-3.



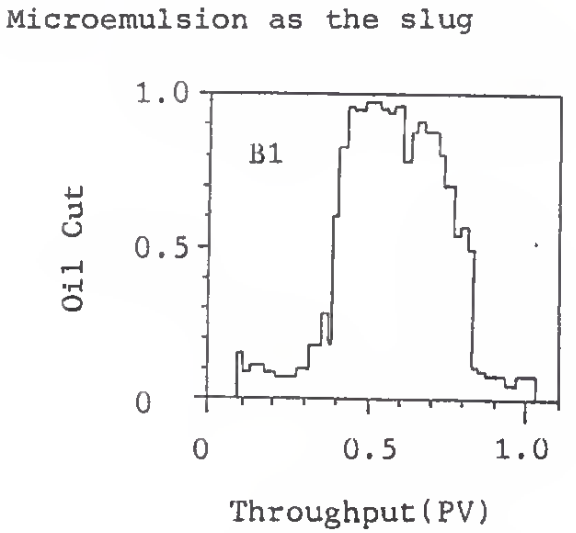


Figure 2-12. Oil production histogram. The composition of the microemulsion slug B1 is represented in Table 2-3.

interesting to examine that effect of injected oil instead of the microemulsion slug. Thus, after water flooding, oil alone was injected as the slug followed by aqueous polymer solution. The results are shown in Table 2-5, Figure 2-11, and Figure 2-12. The oil recovery (52.5%) was almost the same as that for the polymer flooding (48.8%). It should be noticed that we did not obtain better oil recovery using oil as the slug rather than by polymer flooding because the interfacial tension between oil and water was high enough so that oils was re-entrapped giving the same value of the residual oil.

2.6.4 Effect of the Concentration of Salt and Surfactant on Oil Displacement

Effect of Salt Concentration. So far the oil recovery experiments were done using water containing no salt, as shown in Figure 2-13 (a). However, in reality, reservoir water is brine. Since water-in-oil microemulsion, sometimes called soluble oil, decreases its solubilization capacity when water contains salts, previous studies (212) suggested the use of fresh water for tertiary oil recovery. To see the effect of salt on oil displacement, the experiment was modified slightly as shown in Figure 2-13 (b) : brine (2.63% NaCl,W/V) was used initially and for secondary oil recovery. When fresh water was used only for the tertiary oil recovery as suggested by the previous study (212), the oil recovery (72%) was almost equal to that when only fresh water was used for secondary as well as tertiary oil recovery (76.2%), as shown in Figure 2-14.

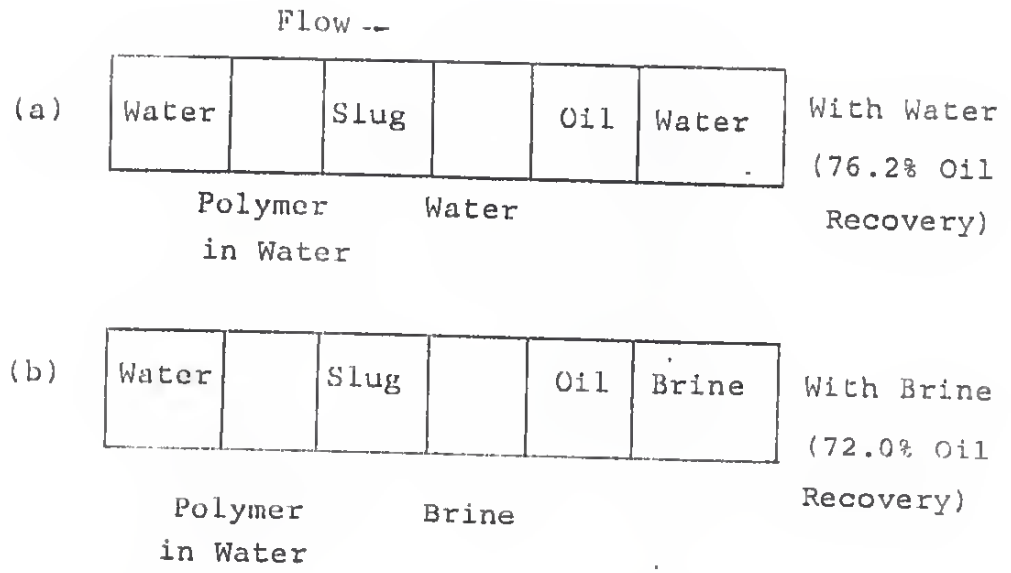


Figure 2-13. A schematic presentation oil displacement experiments. (a) only water was used; (b) brine was used initially and for secondary flooding. The polymer injection employed water rather than brine.

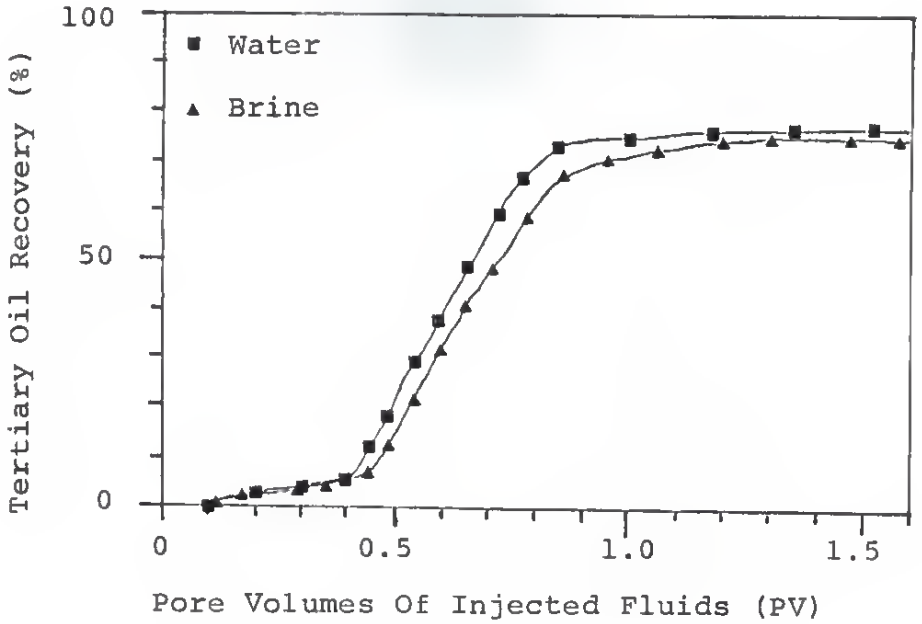


Figure 2-14. Effect of salt on the oil displacement efficiency by the water-in-oil microemulsion slug. The concentration of NaCl in brine was 2.63% (w/v).

Effect of Concentration of Surfactant. When the concentration of the surfactants in the microemulsion slug was reduced by half, oil recovery decreased by about 5%, as shown in Figure 2-15 indicating that reduction in the concentration of surfactants at the optimum weight ratio did not significantly reduced the oil recovery in the range of surfactant concentration employed here.

Oil production histograms were similar for all three experiments except for the oil cut for the experiment with brine as shown in Figure 2-16. A little smaller oil cut was probably a result of a little different relative permeability of oil and brine from that of oil and fresh water.

2.7 Conclusions

1. Alcohol-free microemulsions produced by Aerosol OT, Arlacel 20, mineral oil and water were water-in-oil microemulsions which could solubilize a large amount of water (water-to-oil ratio = 0.83) at the optimal weight ratio of surfactants (AOT : Arlacel 20 = 13 : 27).
2. The oil displacement efficiency was also maximum when the weight ratio of the surfactants was optimum for solubility of water in the w/o microemulsion.
3. The mechanism of oil displacement by the w/o microemulsion is proposed. The surfactants at the optimum ratio exhibited a large solubilization capacity of water which, in turn, produced low interfacial tension and high oil displacement efficiency. Other compositions exhibited a poor solubilization capacity of

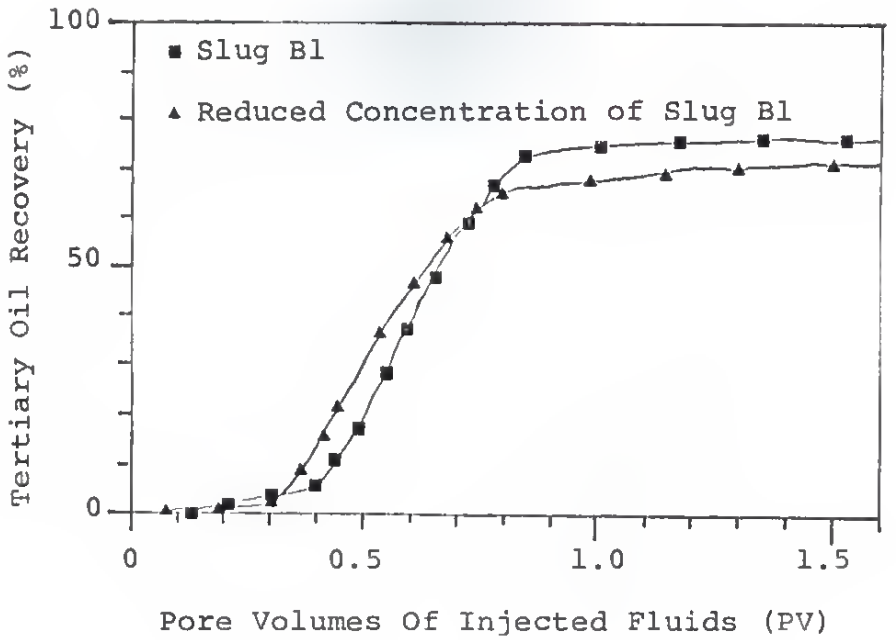


Figure 2-15. Effect of concentration of surfactants in the water-in-oil microemulsion slug on the oil displacement efficiency. Slug B1 contained 0.4 g/ml surfactants and reduced concentration of slug B1 was 0.2 g/ml.

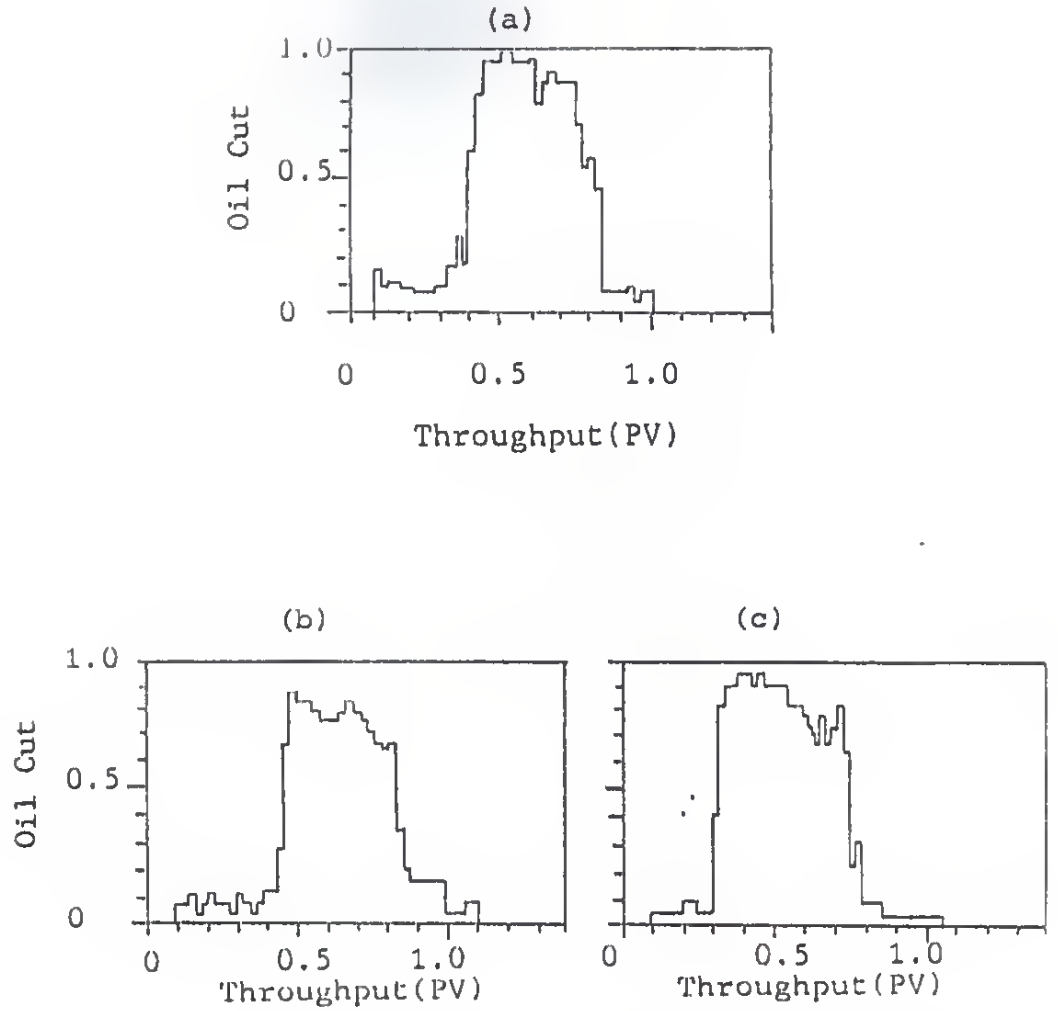


Figure 2-16. Oil production histogram. The concentrations of surfactants in the water-in-oil microemulsion slugs were 0.4 g/ml for (a) and (b) and 0.2 g/ml for (c). The concentrations of salt in the water-in-oil microemulsion slugs were 0% for (a) and (c) and 2.63% NaCl (w/v) for (b).

water and, hence, produced high interfacial tension and poor oil displacement efficiency.

4. The proposed mechanism was in agreement with the results of the oil displacement experiments.
5. The water-in-oil microemulsion consisting of the optimum ratio of the surfactants was very effective with a viscous oil (mineral oil) of which viscosity was 160 cP.

CHAPTER 3

ALCOHOL-FREE MIDDLE-PHASE MICROEMULSIONS

3.1 Introduction

Microemulsions for enhanced oil recovery employ short-chain alcohols as cosurfactants (101, 111, 112, 122, 123, 204, 213, 214). Such short-chain alcohols are believed to introduce fluidity into the system to promote the formation of a microemulsion phase (102, 213). As the salinity of brine increases, the surfactant and the short-chain alcohol in the system solubilize more oil and less brine, resulting in the transition of the microemulsion phase from a lower-phase to an upper-phase through a middle-phase. Among the three different types of the microemulsions, the middle-phase microemulsions have received much attention because of its ultralow interfacial tension with excess oil and brine and high solubilization capacity for both oil and brine (102).

Microemulsions containing short-chain alcohols are not very effective for heavy oil recovery. When long-chain oils ($> C_{14}$) are used, the middle-phase microemulsion containing the short-cbain alcohol does not solubilize much oil or brine (215) as mentioned earlier. Therefore, the volume of the middle-phase microemulsion ia relatively small for heavy oil (109). The reduced solubilization of heavy oil in the middle-phase microemulsion does not lead to

ultralow interfacial tension (216). In addition to high interfacial tension, the reduced solubilization of heavy oil in the middle-phase results in the low viscosity of the middle-phase microemulsion. The low viscosity, then, generates the problem of the mobility control of the slug. A polymer may be added to increase the viscosity of the middle-phase microemulsion. However, the addition of a polymer may cause another problem, incompatibility between a polymer and the surfactant in a slug due to the interaction between polymer and surfactant (101, 217). Further, the phase behavior of the system becomes more complex (217).

The purpose of this study was to show that, by substituting an alcohol with a proper nonionic surfactant, the alcohol-free middle-phase microemulsions could solubilize more oil and produce lower interfacial tension, resulting in a significant improvement in heavy oil recovery. By measuring middle-phase volume and interfacial tension and by performing oil displacement experiments, a comparison can be made between two different middle-phase microemulsion systems, an alcohol-free middle-phase microemulsion and a middle-phase microemulsion containing a short-chain alcohol.

3.2 The Concept of Solubilization

The basic idea of using a nonionic surfactant in the microemulsion arose from Winsor's R theory (102, 218, 219). The theory considered the relative magnitude of the interaction energies of the amphiphile (C) with oil (O) and water (W). The molecular interactions promoting miscibility between C and O and between C and

W are A_{co} and A_{cw}, respectively. The interactions promoting segregation of the components as a separate phase are A_{oo}, A_{ww} and A_{cc}. Winsor proposed that there is a correlation between the mean curvature of the C region and the ratio $R = A_{co} / A_{cw}$. An upper-phase microemulsion is formed when R is higher than one. In contrast, a lower-phase microemulsion is formed when R is lower than one. For a middle-phase microemulsion at optimal salinity, R is one. Bourrel and Chambu (102) modified the expression of R and defined F as follows:

$$F = \frac{A_{co} - 1/2\ (A_{oo} + A_{11})}{A_{cw} - 1/2\ (A_{ww} + A_{hh})} \qquad (3\text{-}1)$$

where A_{11} and A_{hh} are, respectively, the lipophilic- and hydrophilic-type interaction energies between the surfactant molecules. It should be noted that the interfacial interaction energies have to be considered per unit area of interface (102, 220). Since our concern is a middle-phase microemulsion at optimal salinity, equation 3-1 becomes

$$1 = \frac{A_{co} - 1/2\ (A_{oo} + A_{11})}{A_{cw} - 1/2\ (A_{ww} + A_{hh})} \ . \qquad (3\text{-}2)$$

The unity value, F = 1, means that the solubilization parameters of oil and water into the middle-phase are equal. It should be noted

that F = 1 can be obtained as long as the values of the numerator and denominator of F are equal. The solubilization of a middle-phase microemulsion increaaea aa the values of the numerator and denominator of F increase together keeping F = 1 (102).

The reason that the microemulsion does not solubilize a great deal of heavy oil can be explained as follows. Consider the effect of oil chain length on the solubilization capacity. If the chain length of oil increases, A_{oo} increases and A_{co} decreases in equation 3-1. This decreases the value of numerator resulting in F < 1, away from the optimized system. To keep the system optimal, the denominator should also decrease so that F = 1 is maintained. This can be done by decreasing A_{cw} (by increasing the salinity). Thus the optimal salinity increases as the chain length of oil increases if other parametera are fixed. At the same time, the values of denominator and numerator decreaaed together to keep F = 1, reaulting in the decrease of solubilization capacity (102). Therefore, our goal ia to improve solubilization of heavy oil, while maintaining F = 1.

A proper nonionic surfactant can be used as a cosurfactant in place of a short-chain alcohol to solubilize heavy oil. Because of its higher surface activity (102), it does not reduce the aolubilization capacity of the microemulsion. A proper nonionic surfactant can also introduce some degree of disorder into the interface so that gel formation or liquid crystal formation can be avoided.

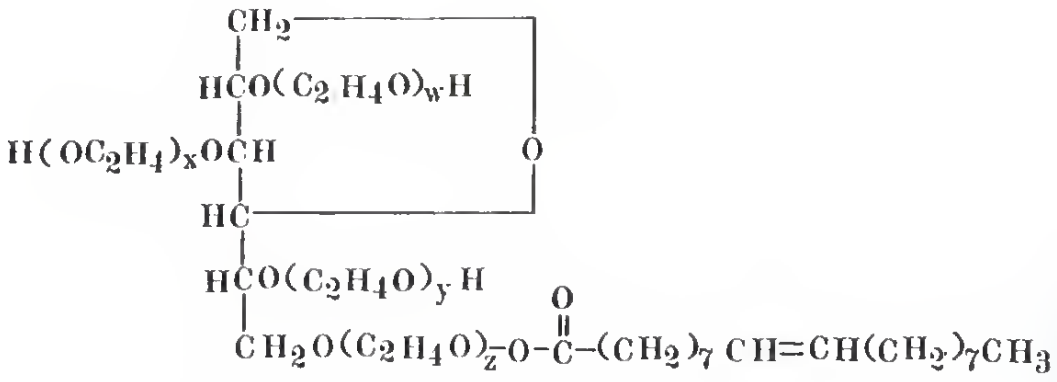
For solubilization, the advantage of using a nonionic surfactant over a short-chain alcohol becomes evident by considering the detrimental effect of a short chain alcohol on the solubilization capacity of the microemulsion (102). Suppose an optimal system is formed by an anionic surfactant alone without using the short-chain alcohol. Then, upon addition of a short-chain alcohol, the alcohol molecules compete with the surfactant molecules to occupy the interface and some of the surfactant molecules are replaced by the alcohol molecules. Thus, A_{co} and A_{cw} in equation 3-1 decrease because the interaction energies are the average of the interaction energies of the surfactant and alcohol molecules (102). Since the values of numerator and denominator decreased together, keeping $F = 1$, the solubilization capacity of the microemulsion decreased upon addition of the alcohol. However, if a proper nonionic surfactant is used in place of a short-chain alcohol, it is possible to maintain high solubilization capacity due to its high surface activity, while maintaining enough interfacial fluidity to form a microemulsion.

3.3 Materials and Methods

All chemicals in this study were used as received without further purification. To prepare the microemulsions or the surfactant solutions, an anionic surfactant (TRS 10-80) from Witco Chemical Company was used with a nonionic surfactant (TWEEN 81) from ICI Americas Inc. or an alcohol (n-butyl alcohol) from Fisher

Scientific Company. TRS 10-80 was a commercial petroleum sulfonate having an average molecular weight of 426. TWEEN 81 was polyoxyethylene 5 sorbitan monooleate having a molecular weight of 664 and HLB value of 10. The structure of TWEEN 81 is shown in Figure 3-1. N-butyl alcohol (NBA) was a certified grade. To simulate heavy oil, mineral oil was used throughout the study as described in Chapter 2. De-ionized, distilled water was used to prepare brine. Sodium chloride from Fisher Scientific Company was a certified A.C.S grade.

Solubilization and optimal salinity of the middle-phase microemulsions were measured using graduated cylinders. Two different stock solutions were first prepared by dissolving 10% (w/v) TWEEN 81 or 10% (w/v) n-butyl alcohol with 10% (w/v) TRS 10-80 in mineral oil. The stock solution was then mixed with the same volume of brine at different salinity. The mixed samples were vigorously shaken and put on a rotator for 24 hours before putting them into an incubator to allow phase equilibrium. Phase equilibrium was checked by monitoring volume change of each phase. When the equilibrium was reached, solubilization was measured which was the volume of oil and brine solubilized in the microemulsion phase. Optimal salinity was the salinity at which the same volume of oil and brine was solubilized in the middle-phase microemulsion (101, 123, 204). Interfacial tension (IFT) was measured by a spinning-drop tensionmeter after phase equilibrium was reached. Both the theory and experimental methods employed here have been well described in the previous studies (124, 221).



X + Y + W + Z = 5

Figure 3-1. Structure of Tween 81.

Oil recovery experiments were performed using sand packs, 2 ft in length and 0.95 in. in diameter. A sand pack had an average porosity of 0.38 and an average absolute permeability of 6.5 darcies. The typical relative permeability of mineral oil and brine through a sand pack for this study is shown in Figure 3-2.

When more than one fluid simultaneously flow through a porous medium, their flowing velocities through the porous medium are determined by their viscosities and relative permeabilities. Therefore, the information about the relative permeabilities of oil and brine are very important to estimate the proper viscosity of the microemulsion slug. To find oil and water relative permeabilities by the unsteady-state method (222), a porous medium is saturated with water and is, then flooded to irreducible water saturation by oil. Subsequently, the porous medium is again flooded by water at different flow rates of water. Pressure drops across the porous medium at different flow rates of water are determined. Effluent fractions are collected and the amount of water and oil in each effluent fraction is determined. With the absolute permeability, pore volume of the porous medium, and viscosities of oil and water, these data are then used to calculate the relative permeabilities of oil and water through the porous medium.

The experimental procedure of oil recovery was as follows. First, a sand pack was conditioned by saturating it with carbon dioxide to displace air. The sand pack was then flooded with about 10 pore volumes (PV) of brine having optimal salinity. During the

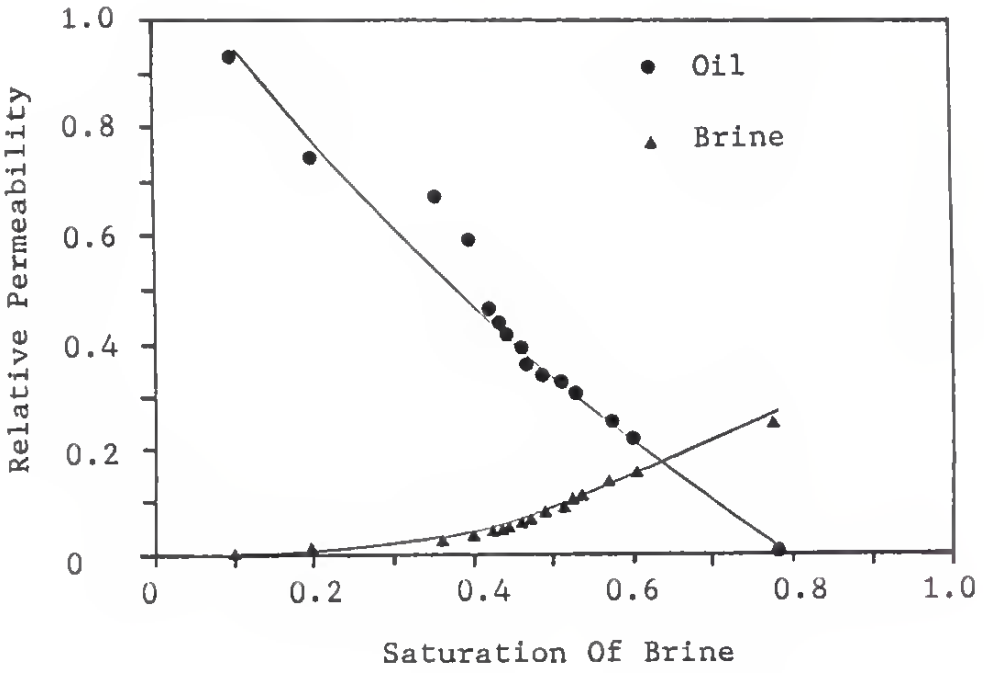


Figure 3-2. Relative permeability curve. Oil was mineral oil and brine was 2.63% NaCl.

brine flooding, PV and absolute permeability of the sand pack were measured using a material balance and measuring the slope of the straight line obtained from data of flow rate and pressure difference, as shown in Figure 3-3, respectively. After the brine flooding, the saturated brine was displaced by mineral oil. Mineral oil was injected until no brine was produced. An average oil saturation was 92.6%. The saturated oil was then displaced by brine at different flow rates to measure a relative permeability by the unsteady-state method (secondary oil recovery) (222). Secondary oil recovery waa diacontinued when the production ratio of oil to brine was less than 0.01 in a produced sample. An average secondary oil recovery for the mineral oil was 63%. The remaining oil after aecondary oil recovery was displaced at 1 ft/day by the slug, the middle-phase microemulsions or the aurfactant aolution for the tertiary oil recovery. Since our purpose was to compare two different systems, a large volume of the slug (about 1.0 PV) was injected without using any mobility buffer (e.g., polymer solution) to displace the surfactant slug. In three separate experiments, three different slugs were used : (1) the alcohol-free middle-phase microemulsion containing TRS 10-80 and TWEEN 81, (2) the middle-phaae microemulsion containing TRS 10-80 and NBA, and (3) the aqueous alcohol-free aurfactant solution containing TRS10-80 and TWEEN 81 for in-situ generation of the alcohol-free middle-phase microemulsion (103, 223, 224).

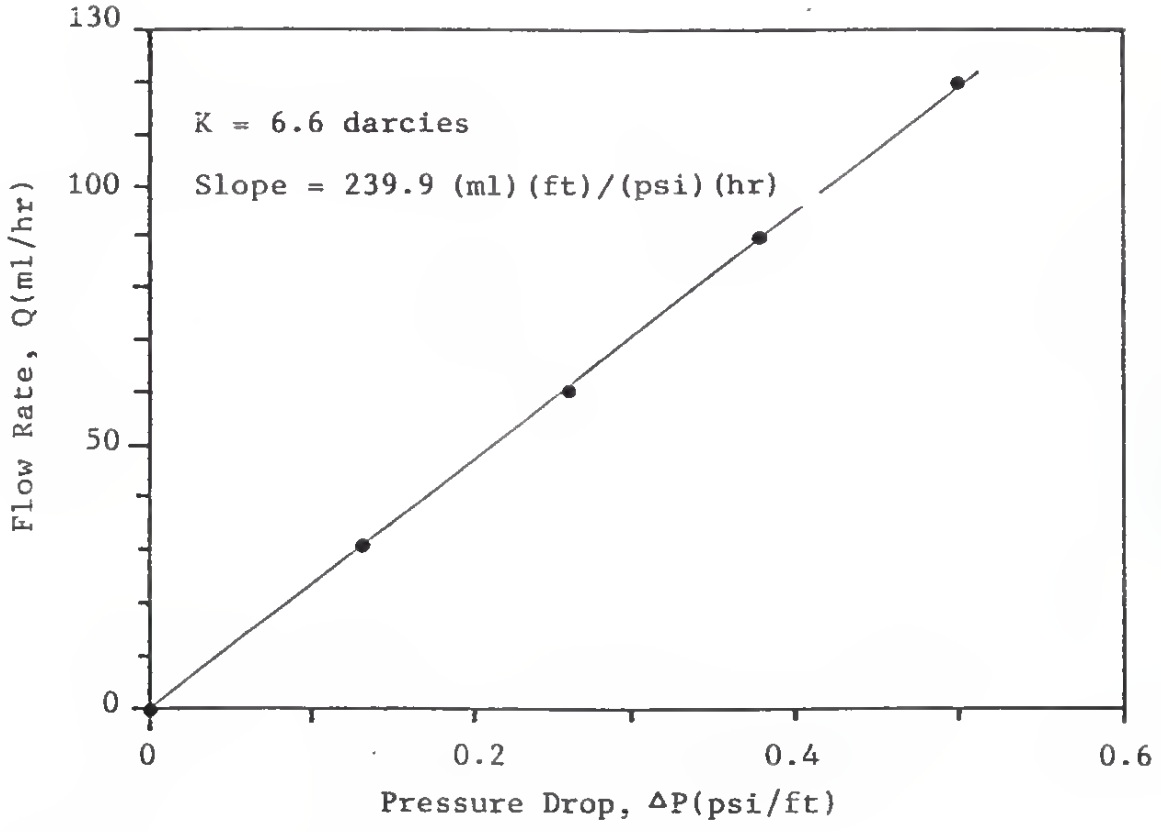


Figure 3-3. Flow rate depending on pressure drop for the measurement of absolute permeability. Slope equals to K ΔP / μ A where K = absolute permeability, μ = viscosity of displacing fluid, A = cross-sectional area of sand pack and ΔP = pressure drop per unit length of the sand pack.

3.4 Results and Discussion

According to the concept of solubilization described earlier, middle-phase microemulsion containing a short-chain alcohol cannot solubilize much heavy oil. However, the alcohol-free middle-phase microemulsion can solubilize enough heavy oil to lower IFT without forming a gel if a proper nonionic surfactant ia used in place of the short-chain alcohol. Therefore, the purpose of the study was to compare two different middle-phase microemulsions, one with a short-chain alcohol and the other with a nonionic surfactant in place of a short-chain . alcohol. In order to compare the two systems, an anionic surfactant (TRS 10-80) was used to prepare both systems. The only difference between the two systems was the selection of the cosurfactant, i.e. normal butyl alcohol (NBA) or TWEEN 81. Several alcohols were tested and, among them, NBA was chosen because NBA gave its middle-phase microemulsion almost the same optimal salinity (2.80% NaCl) as that of the alcohol-free middle-phase microemulsion (2.63% NaCl).

3.4.1 Solubilization and Optimal Salinity of Middle-Phase Microemulsions

Figures 3-4 and 3-5 show the solubilization and optimal salinity of the two systems. Optimal salinities of the systems containing NBA and TWEEN 81 were 2.80% NaCl (w/v) and 2.63% NaCl (w/v), respectively. The solubilization of oil and water into the middle phase waa expressed as total volume of middle phase per unit amount of surfactants used, i.e. TRS 10-80 plus NBA or TRS 10-80

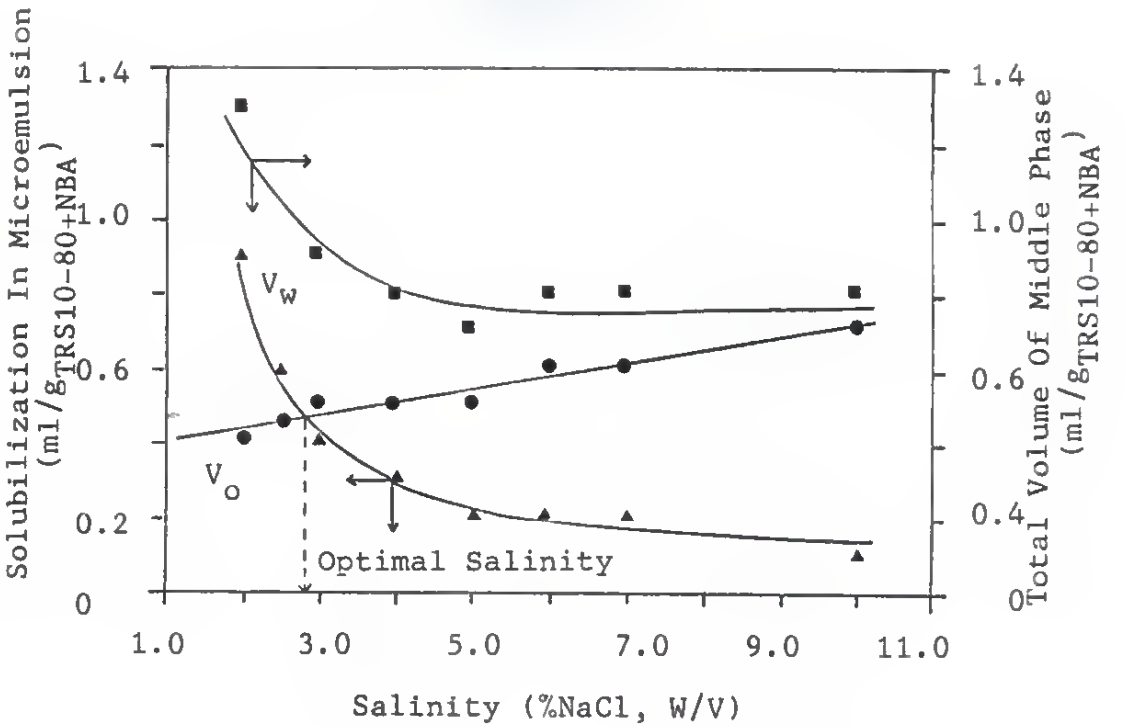


Figure 3-4. Solubilization and optimal salinity of the middle-phase microemulsion containing n-butanol. Mineral oil contained TRS 10-80 (10%, w/v), n-butanol (10%, w/v); WOR = 1.0.

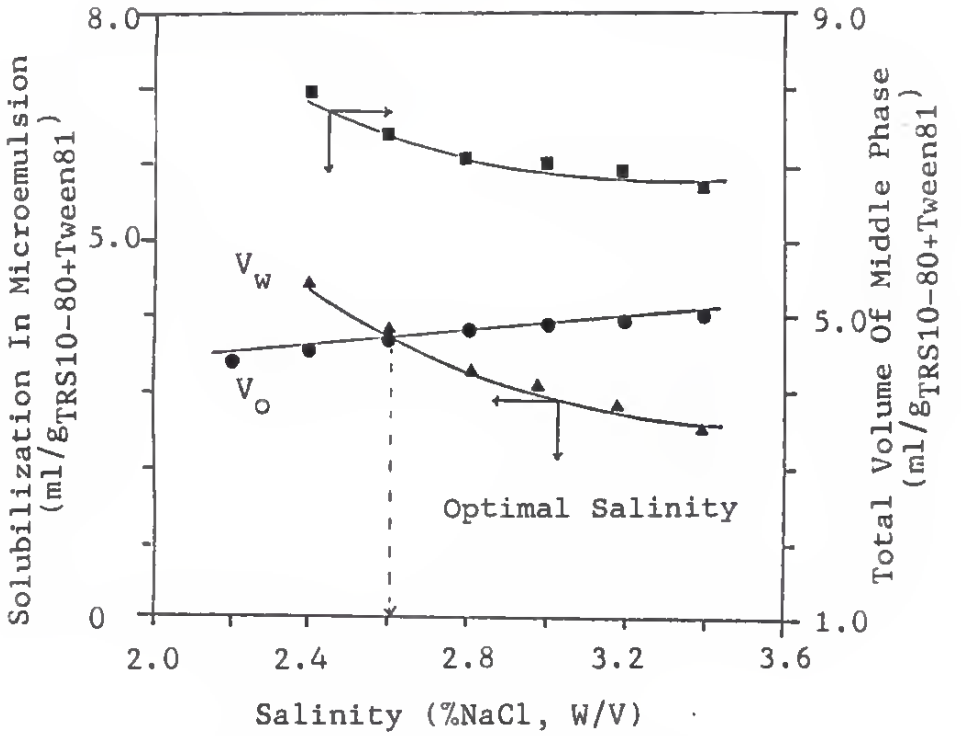


Figure 3-5. Solubilization and optimal salinity of the alcohol-free middle-phase microemulsion. Mineral oil contained TRS 10-80 (10%, w/v), Tween 81 (10%, w/v); WOR = 1.0.

plus TWEEN 81. The total volume of the middle phase was much larger for the alcohol-free middle-phase microemulsion than for the middle-phase microemulsion containing NBA. At optimal salinity, the volume of the middle phase for the microemulsion containing TWEEN 81 was about 8 times larger than that for the microemulsion containing NBA. It should be noted that a wide range of salt concentration must be used to find the optimal salinity of the system containing NBA because the microemulsion cannot solubilize much oil by increasing salinity. In contrast, a limited range of salt concentration was used to find the optimal salinity of the system containing TWEEN 81 because of its ability to solubilize much of the oil compared with the system containing NBA. These observations definitely support the concepts of solubilization on which this study was based: When heavy oil is used, the solubilization of heavy oil and water in the middle-phase mecroemulsion can be increased by substituting a short-chain alcohol with a proper nonionic surfactant. The microemulsion phases for both systems were clear and fluid without the formation of any gel or liquid crystals. In addition to IFT, a proper viscosity of the microemulsion is another important property for good oil recovery (117). Poor solubilization of heavy oil in the microemulsion may not produce enough viscosity to displace heavy oil due to channeling phenomena. Addition of polymer can introduce other problems as mentioned earlier. Viscosities of the microemulsions were measured to see the effect of oil. At the corresponding optimal salinities, viscosities of the microemulsions

with NBA and TWEEN 81 were 37 cP and 210 cP, respectively, compared to 160 cP for the mineral oil used in the study.

As mentioned earlier, isobutanol, isopentanol, n-pentyl alcohol and n-octyl alcohol were tested before choosing NBA. It should be mentioned here that solubilization behavior of these alcohols was similar to NBA (i.e., small solubilization of oil and/or water). Among those alcohols, n-pentyl alcohol and n-octyl alcohol formed only upper-phase microemulsions in the salinity range of 1.0 to 10.0% NaCl.

3.4.2 Interfacial Tension

Many efforts have been made to formulate a microemulsion system which has a greater solubilization capacity (71, 102). It is known that high solubilization is a requirement for producing low IFT (71, 217). Measurements of IFT for the two different microemulsion systems showed that large solubilization was required for low IFT. Figures 3-6 and 3-7 show IFT as a function of salinity for the two different systems. Indeed, IFT of the alcohol-free middle-phase microemulsion containing TWEEN 81 was lower by an order of magnitude than that of the middle-phase microemulsion containing NBA at the optimal salinities. Both systems had the lowest IFT at their optimal salinities. It is interesting to note that interfacial tensions of microemulsion/brine and oil/microemulsion interfaces were not equal for both systems at optimal salinity even though their interfacial tensions were lowest at this point. A similar phenomenon was observed by Gupta and Trushenski (201).

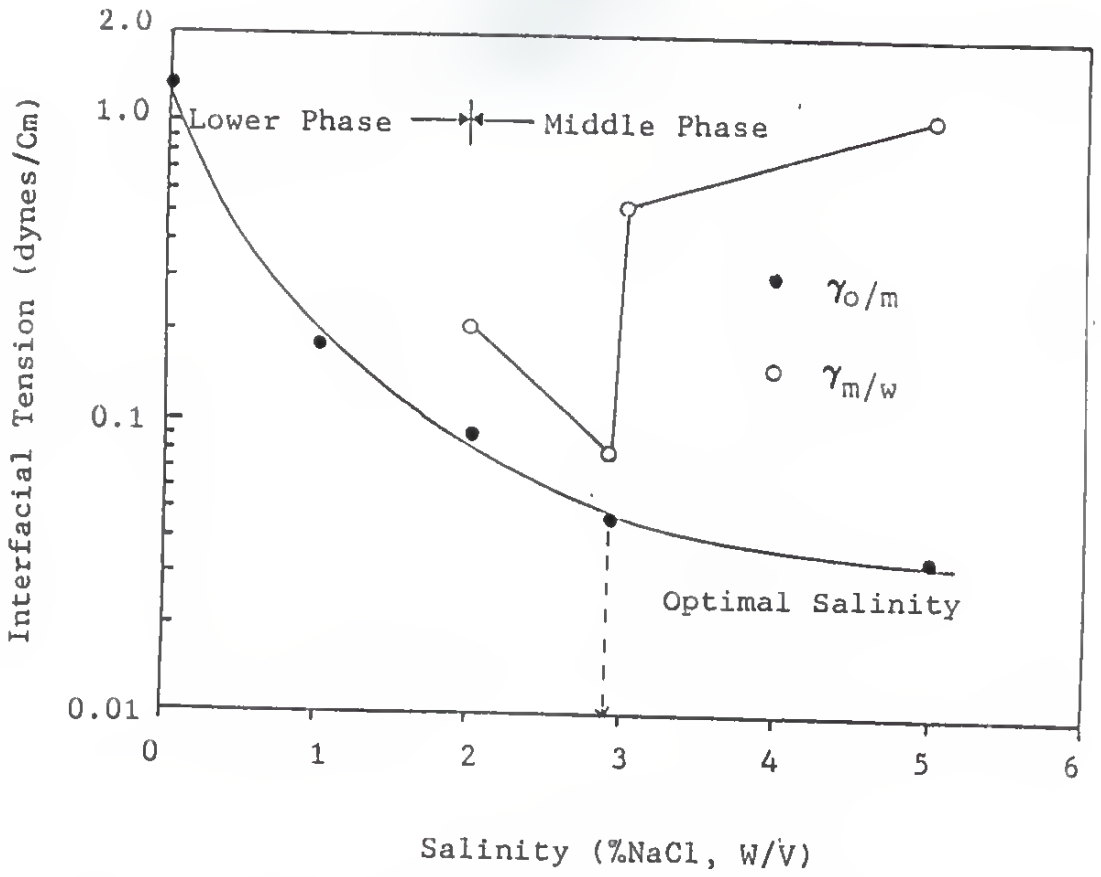


Figure 3-6. Interfacial tension of the middle-phase microemulsion containing n-butanol with excess oil or brine phase. Mineral oil contained TRS 10-80 (10%, w/v), n-butanol (10%, w/v); WOR = 1.0.

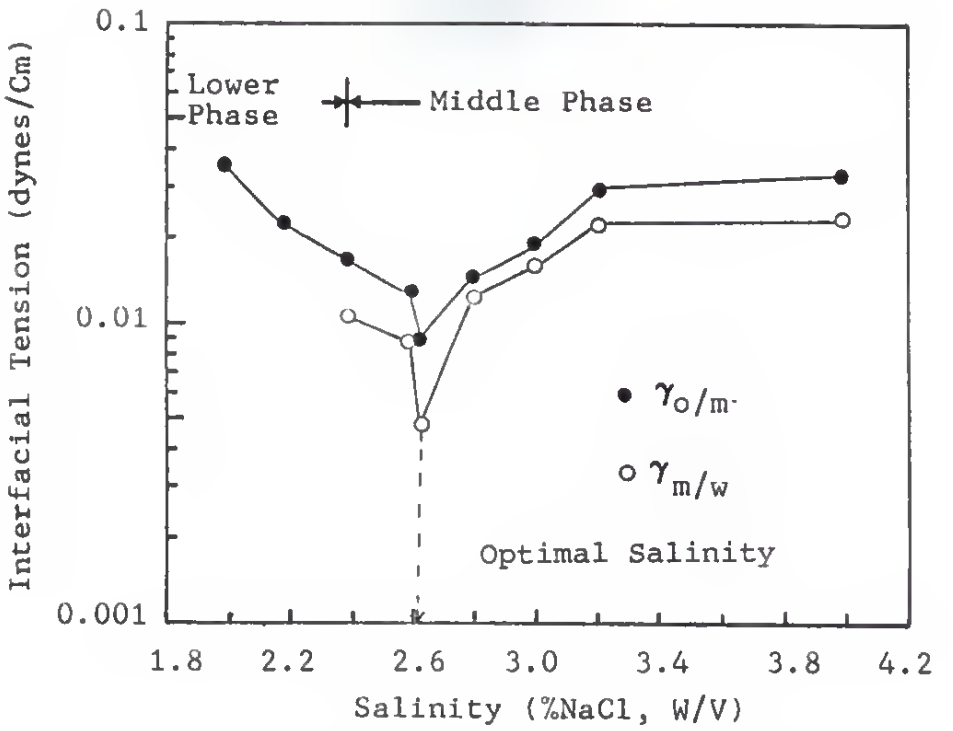


Figure 3-7. Interfacial tension of the alcohol-free middle-phase microemulsion with excess oil or brine phase. Mineral oil contained TRS 10-80 (10%, w/v) and Tween 81 (10%, w/v); WOR = 1.0.

3.4.3 Oil Displacement Efficiency

Three different slugs were used for tertiary oil recovery experiments. Two of them were middle-phase microemulsions with NBA (slug A) and with TWEEN 81 (slug B) respectively. The third (slug C) was a surfactant solution without oil, i.e. the mixture of TRS 10-80, TWEEN 81 and brine so that the middle-phase microemulsion could be formed in-situ.

The results are shown in Table 3-1 and Figure 3-8, and agreed well with data from solubilization, viscosity and interfacial tension measurements. Tertiary oil recoveries were 98% for the slug C, 88% for the slug B and 39% for the slug A. The poor oil recovery for the slug A resulted from high IFT and poor mobility control due to the low viscosity of the slug. While the sudden increase in oil production for the slugs A and B started at the same volume of the slug injections at 0.5 PV, oil recovery leveled off faster for the slug A than for the slug B. The oil production histogram in Figure 3-9 showed that the oil cut sharply decreased for slug A at 0.6 PV presumably due to early invasion of the slug into the formed oil bank. Two different heights in the oil cut (at 0.55 PV and 0.7 PV) were obtained for slug A, while a single sudden increase in oil cut was obtained for the slug B. This supports the assumption that some of the slug A bypassed the residual oil (111). The higher oil cut of the oil bank for slug B (0.9) than slug A (0.75) implies the lower IFT of the slug B resulting in release of trapped residual oil

Table 3-1. Efficiency of Oil Displacements Using Middle-Phase Microemulsions

Slug	PV[a]	Oil[b] Saturation		Secondary[c] Oil Recovery		Residual[c] Oil		Tertiary[d] Oil Recovery	
	(ml)	(ml)	(%)	(ml)	(%)	(ml)	(%)	(ml)	(%)
A[e]	100	93	93	62.0	67	31.0	33	12.1	39
B[f]	105	99	94	56.5	57	42.5	43	37.2	88
C[g]	105	95	91	62.0	65	33.0	35	32.3	98

a. Pore volume of sand pack.

b. Calculated based on the pore volume of sand pack.

c. Calculated based on the saturation of oil.

d. Calculated based on the residual oil after water flooding.

e. The middle-phase microemulsion was prepared by equilibration of the equal volume of mineral oil and brine which contained 10% TRS10-80, 10% n-butanol and 2.80% NaCl (W/V).

f. The middle-phase microemulsion was prepared by equilibration of the equal volume of mineral oil and brine which contained 10% TRS10-80, 10% Tween 81 and 2.63% NaCl (W/V).

g. Surfactant solution containing 10% TRS10-80, 10% Tween 81 and 2.63% NaCl (W/V): the middle-phase microemulsion was formed in-situ.

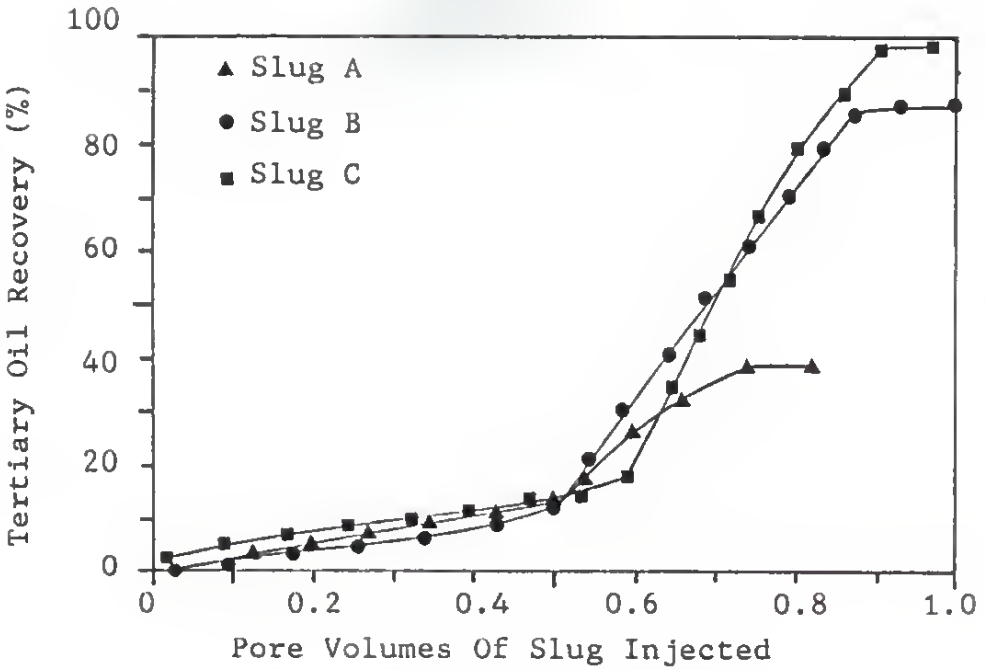


Figure 3-8. Oil displacement efficiency. Slug A is the middle-phase microemulsion containing n-butanol; slug B is the alcohol-free middle-phase microemulsion; slug C is the alcohol-free surfactant solution resulting in the in-situ formation of middle-phase microemulion.

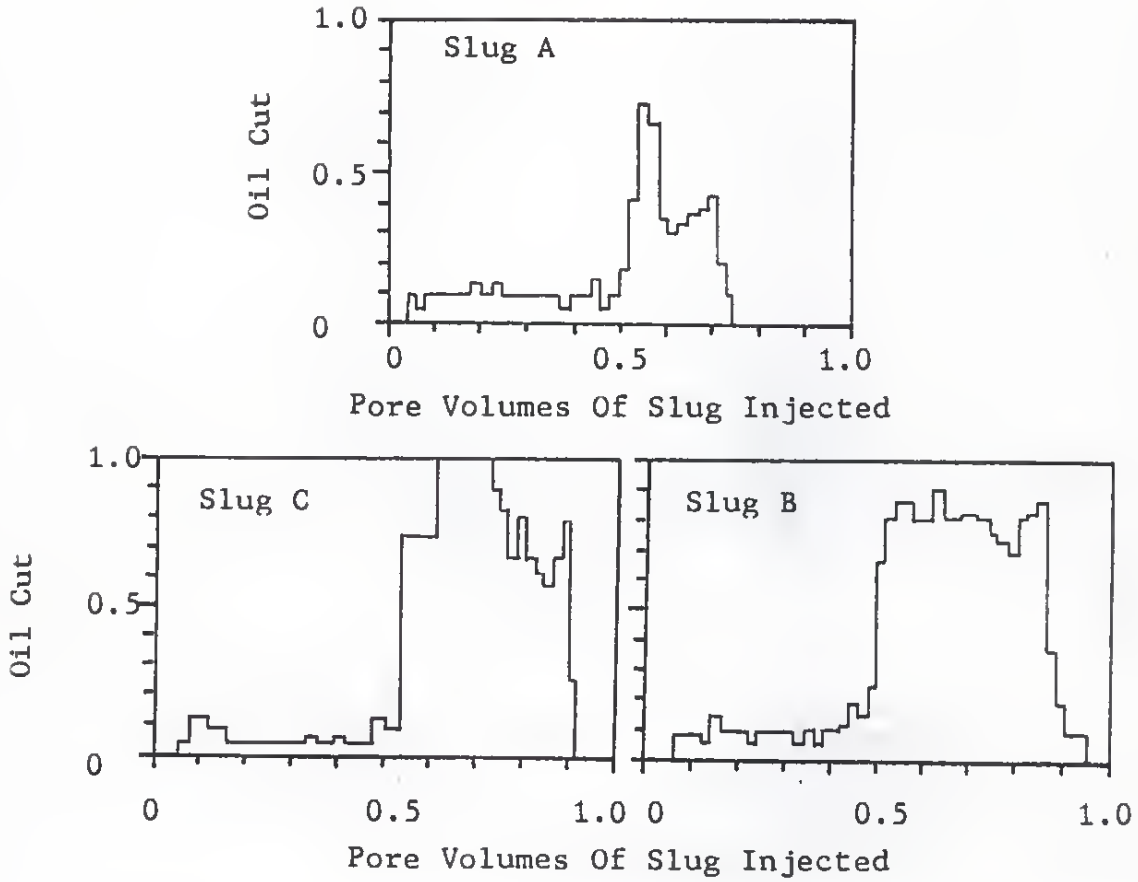


Figure 3-9. Oil production histogram. Slug A is the middle-phase microemulsion containing n-butanol; slug B is the alcohol-free middle-phase microemulsion; slug C is the alcohol-free surfactant solution resulting in the in-situ formation of the middle-phase microemulsion.

and rapid coalescence of the released oil (122). Tertiary oil recovery by the alcohol-free middle-phase microemulsion formed in-situ was the best, 98%, among the three different slugs, implying piston-like displacement by the alug C. The better performance of slug C might result from apontaneoua aolubilization of residual oil which, in turn, resulted in the miscible diaplacement of residual oil during the in-situ formation of the middle-phase microemulsion in contrast to the immiacible diaplacement of the residual oil by Slug B. Oil recovery experiments and reaulta are schematically summarized in Figure 3-10.

3.5 Conclusions

1. The alcohol-free middle-phase microemulsion was succesafully formulated, by substituting the alcohol (NBA) with the nonionic aurfactant (TWEEN 81) aa the cosurfactant without forming gel or liquid crystals, based on the Winsor'a R theory.
2. The solubilization capacity of the alcohol-free middle-phase microemulsion was much greater than that of the middle-phase microemulsion containing short-chain alcohola (C_3-C_6).
3. The IFT of the alcohol-free middle-phase microemulsion was lower by an order of magnitude than that of middle-phase microemulaion containing the short-chain alcohol.
4. The alcohol-free middle-phase microemulsion waa much more effective for heavy oil recovery (88-98%) than the middle-phase microemulaion containing the short-chain alcohol (39% oil recovery) due to increaaed solubilization of heavy oil and

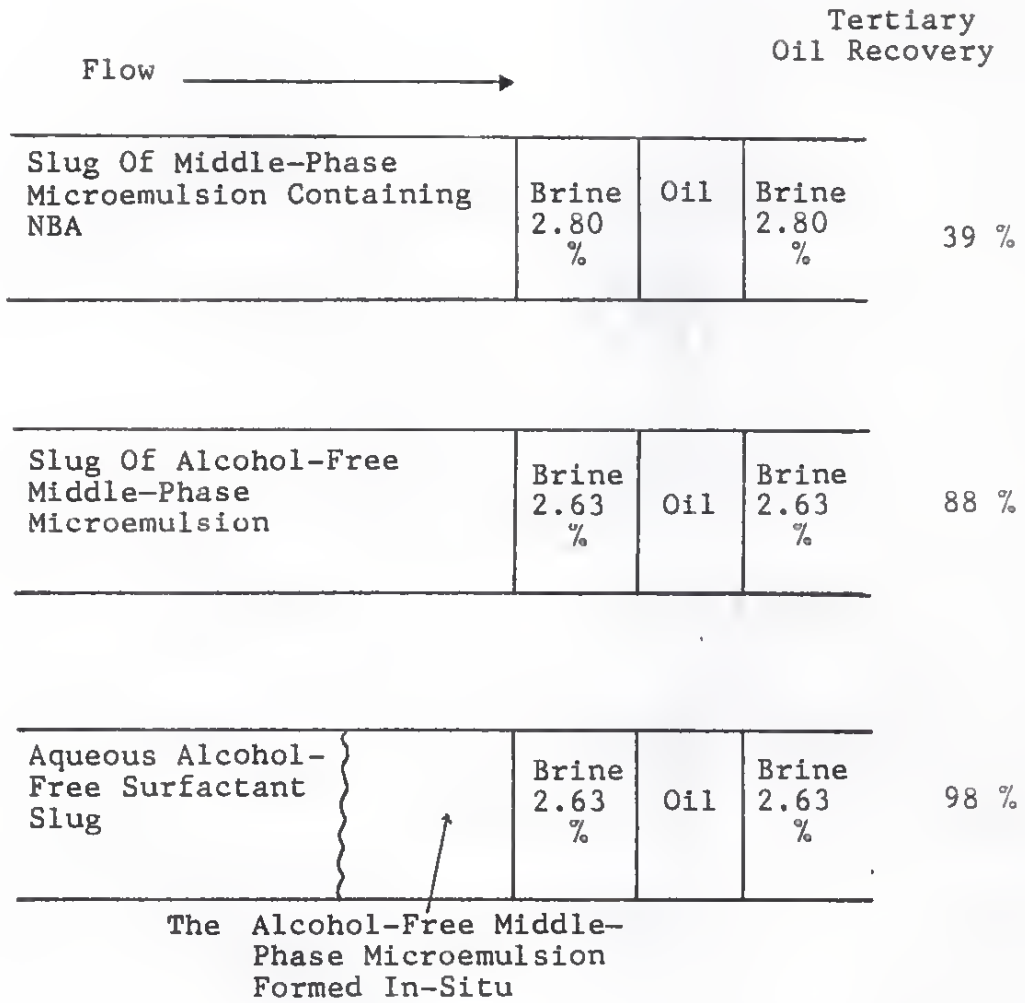


Figure 3-10. A schematic presentation of the microemulsion flooding and percent oil recovery. The compositions of the slug are represented in Table 3-1.

brine, lower IFT and a proper viscosity due to the presence of the nonionic surfactant.

CHAPTER 4

EXCLUDED VOLUME EFFECT OF ANIONIC POLYMERS ON ANIONIC SURFACTANT SOLUTIONS

4.1 Introduction

The effect of a polymer on a surfactant in aqueoua solution has received considerable attention because of its biological, pharmaceutical, mineral proceasing and oil recovery applications (116, 129, 225, 226). It has been mentioned in an earlier chapter that the addition of polymer into the surfactant solution alters the interfacial and rheological properties of the surfactant such as aolubilization (134, 136, 142), conductivity (135, 136), surface tenaion (135, 142, 146) and viscoaity (132, 134, 135) for the nonionic polymer-ionic aurfactant systems. Previoua investigators (132, 134-136, 142, 146) explained these unusual properties of the aurfactant solution upon the addition of the polymer by the formation of a complex between the polymer and the aurfactant or the formation of the micellea inaide the polymer coila. It haa been shown that auch a complex was formed by the adsorption of the nonpolar tail part of the ionic aurfactant on the polymer and the polar head to the aqueous phase (132). Later, it waa ahown that the electrical forces between the polymer and the aurfactants were alao important, in addition to hydrophobic bonding (142). However, the known nature of such anionic polymers as polyacryamides and xanthan

(the great hydrophilicity and the lack of strongly hydrophobic moieties in their structures), it is difficult to conceive that hydrophobic effects play any significant role in the interaction with anionic surfactants such as petroleum sulfonates and sodium dodecyl sulfate (SDS). In addition, the anionic nature of both surfactants and polymers makes it difficult to believe that these can associate due to Coulombic forces. The above discussion leaves question the mechanism of interaction between anionic polymer and the anionic surfactant. Desai (116) has shown that the same phenomena of lowering surface and interfacial tensions occurred for anionic polymer-anionic surfactsnt systems.

Even though Desai (116) did not recognize the difference in the pattern of the change in surface tension as a function of surfactant concentration between his system (anionic polymer-anionic surfactant) and the systems in the previous systems (nonionic polymer-ionic surfactant), it can be seen that, for an anionic polymer-anionic surfactant system, the pattern of the decrease in surface tension was much different from that reported in the previous studies (135, 136, 142) suggesting that the formation of the complex between the polymer and the surfactant was not responsible for the decrease in the surface tension for the anionic polymer-anionic surfactant systems used in his study. The dialysis measurements also supported this conclusion (116).

Desai (116) proposed the excluded volume effect of anionic polymer on anionic surfactant solution to explain the lowering

surface and interfacial tenaion for an anionic polymer-anionic surfactant aystem. Even though his proposed mechaniam was sound, no experimental evidence except the dialysis measurementa waa provided. The excluded volume effect by the polymer on the surfactant waa investigated for an anionic polymer-anionic surfactant ayatem using the light acattering technique to verify Desai's proposed mechanism and to predict the effect of polymer on surface and interfacial tension in this study. Using the effective concentration of the surfactant in a polymer solutiona obtained by the calculated excluded volume effect, interfacial and aurface tension values were obtained from the experimental data for an anionic surfactant system without polymer and were compared to the experimental values of interfacial and and aurface tensions for the mixed anionic polymer-anionic surfactant system.

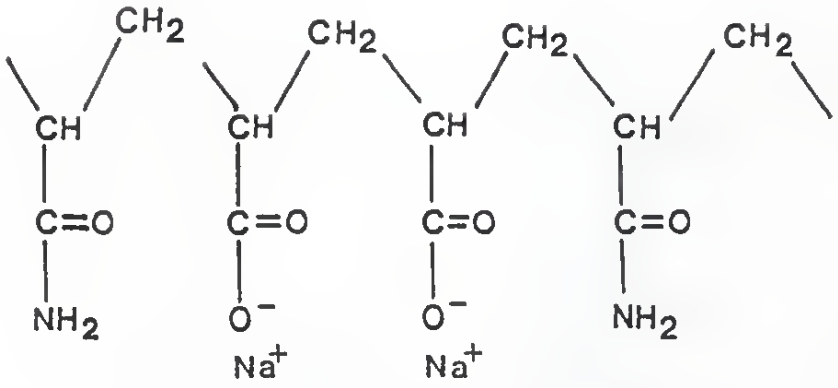
The effect of the anionic polymer-anionic surfactant interaction on the lowering interfacial tension was further investigated by oil displacement experiments, which were performed uaing a modified polymer solution by addition of a very small amount of a surfactant. As expected, the modified polymer solution most effectively displaced the residual oil when compared to the polymer solution alone and the surfactant solution alone, confirming the exiatence of the ultralow interfacial tension in the mixed polymer-aurfactant systems.

4.2 Materials and Methods

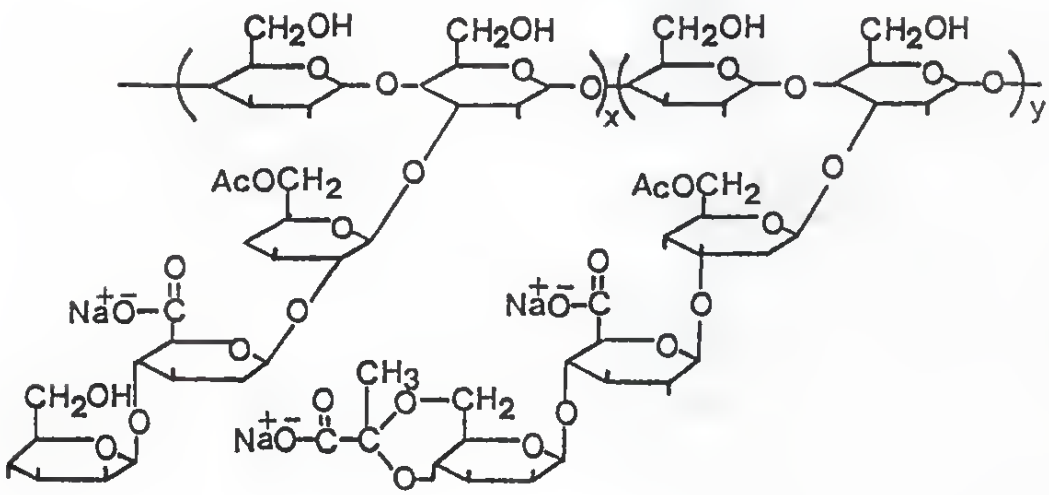
TRS 10-80 used in this study waa the aame as that deacribed in Chapter 3. Sodium dodecyl sulfate (SDS) was obtained from Research Organic Inc. Normal hexane used in thia atudy was obtained from Phillips Petroleum Company and waa 99% pure. The anionic aynthetic polymers were two polyacrylamides having the different degrees of hydrolysia and were obtained from Calgon Corporation. Their commercial names are Calgon 800 and Calgon 835. Calgon 835 was more hydrolyzed than Calgon 800. The anionic biopolymer was high-pyruvate Xanthan from Pfizer, Inc. and its commercial name is FLOCON 4800. The chemical structures of the polymera are shown in Figure 4-1.

Surface tension was measured by the Wilhelmy plate method (18) using a Roller-Smith precision balance (model L.G.) with a platinum blade sandblasted for increased wettability. Samples were taken in a Petri-dish and kept covered for one hour, with the surface undisturbed, before measurementa.

Dynamic (quasi-elastic) and static light scattering measurements were performed with a Spectra Phyaic argon ion laser (series 2000), Brookhaven laser light scattering goniometer (BI-200SM), and Brookhaven digital correlator (BI 2030) at 514.5 nm, 90 degree angle and 25 ^{o}C. The effective diameters of the polymer molecules were obtained from the diffusion coefficients meaaured at different concentrationa of the polymer by quasi-elastic light acattering (QELS) using the Stokes-Einstein relationahip (227):



Polyacrylamides



High-pyruvate Xanthan

Figure 4-1. Structures of anionic polymers.

$$D = k\,T\,/\,(3\ \eta\ d) \qquad (4\text{-}1)$$

where $k = 1.38054 \times 10^{-16}$ erg/K, Boltzmann's Constant

T = absolute temperature in K

η = viscosity of diluent

d = particle diameter.

The static light scattering (SLS) technique was used to obtain the second virial coefficient. The molecular weight and the second virial coefficient were obtained from the intercept and the initial slope, respectively, of the plot, $K\,C\,/\,R_\theta$ vs. C using the Debye's equation (228):

$$K\,C\,/\,R_\theta = 1\,/\,M + 2\,B\,C + \text{----------} \qquad (4\text{-}2)$$

where $K = (2\,\pi^2\,/\,L\,\lambda^4)\,(n_o)^2\,(dn/dC)^2$

C = concentration of the macromolecule

R_θ = Rayleigh ratio = $(i_\theta\ /\ I_\theta\ )\,(r^2\,/\,2\,SIN^2\,\theta)$

M = molecular weight of the macromolecule

B = second virial coefficient

L = Avogardro's number

λ = Wave length

n = refractive index of the solution

n_o = refractive index of the solvent

i_θ = the scattered intensity per unit volume

I_θ = the incident light intensity

θ = scattering angle.

The necessary refractive index was measured by a Spencer refractometer at 25°C: n_o and dn/dC were 1.3347 and 0.131 cm^3/g, respectively. The results are shown in Figure 4-2 for Calgon 800 polymer solution. Before the refractive index and SLS experiments, the polymer solutions were made dust free by centrifugation for 5 hours at 3000 g using International Clinical Centrifuge (Model CL) from International Equipment Co. snd filtration through the 0.3 μm filter.

4.3 Effect of Addition of Polymers on Interfacial and Surface Tension

As indicated by the dotted line in Figure 4-3, the polymer itself did not have any surface activity (116). This is not surprising because of the strongly hydrophilic nature of polyacrylamide. Therefore, it should be noted that, in this study, the effect of a non-surface active polymer on surfactants in the solution was investigated. Also, as shown in Figure 4-4, the surfactant alone did not decrease the interfacial tension (IFT) without the polymer at the low concentration such as 0.002% (w/v). However, as shown in Figure 4-3, at the same low concentration of the surfactant, the IFT dramatically decreased upon adding the polymer, and the effect of the polymer reduced at the high concentrstion of the polymer. Figure 4-4 shows that the effect of

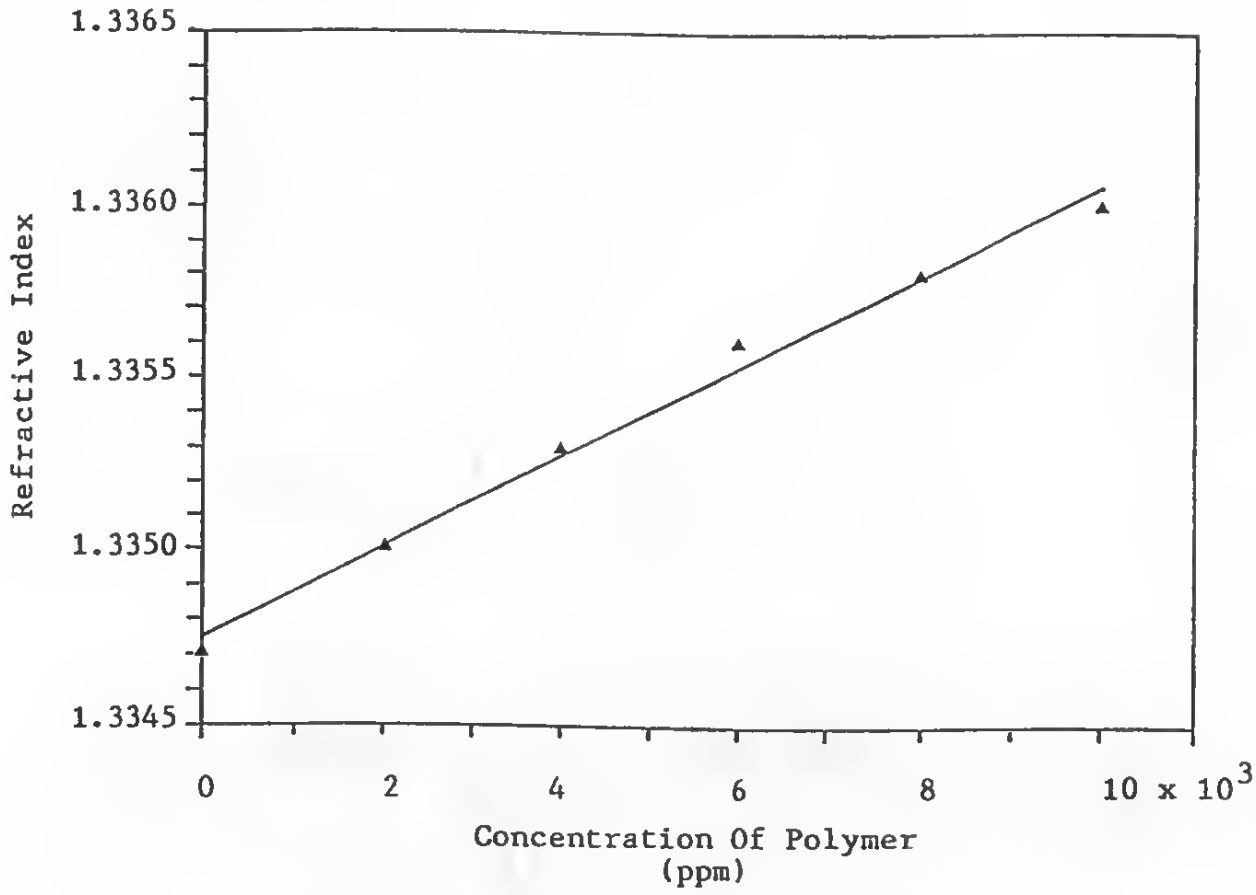


Figure 4-2. Refractive index of polymer, Calgon 800.

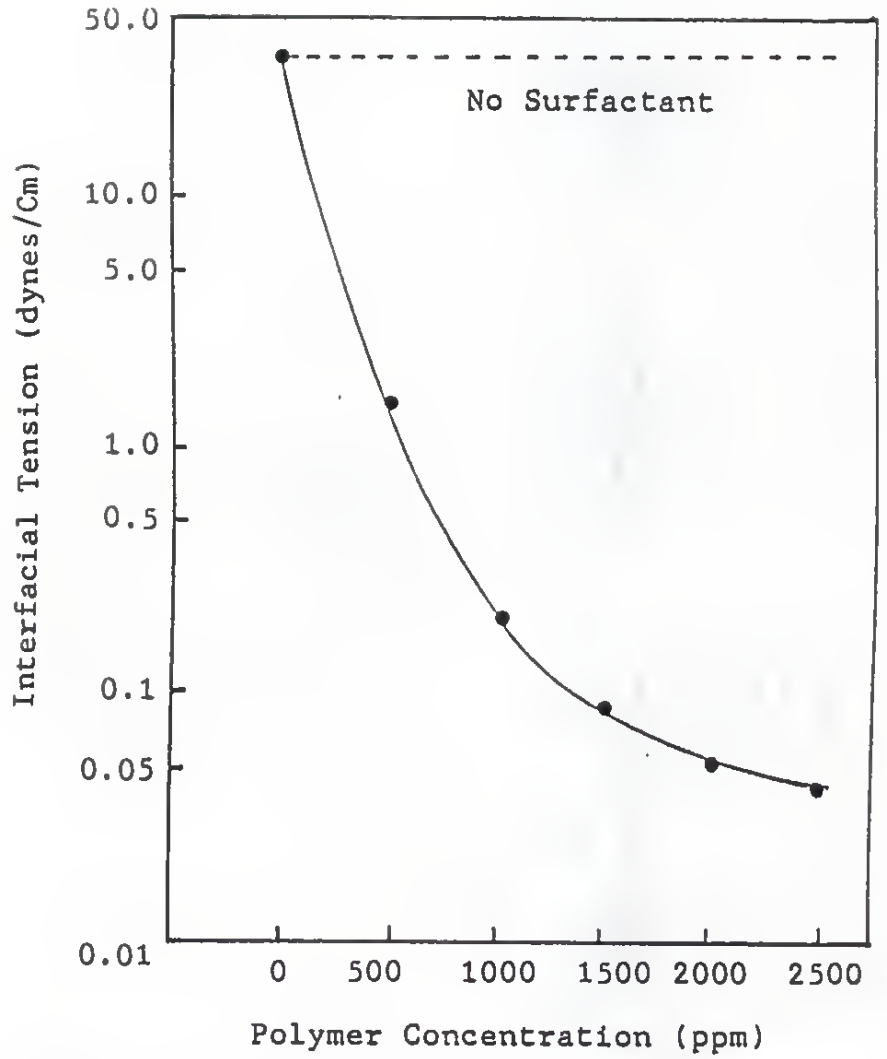


Figure 4-3. Effect of polymer concentration on interfacial tension against n-hexane. Brine (1.0% NaCl, w/v) contained TRS 10-80 (0.002%, w/v) and Calgon 800. WOR = 1.0. Taken from Desai, N., Ph.D. dissertation, p.38, University of Florida, 1983.

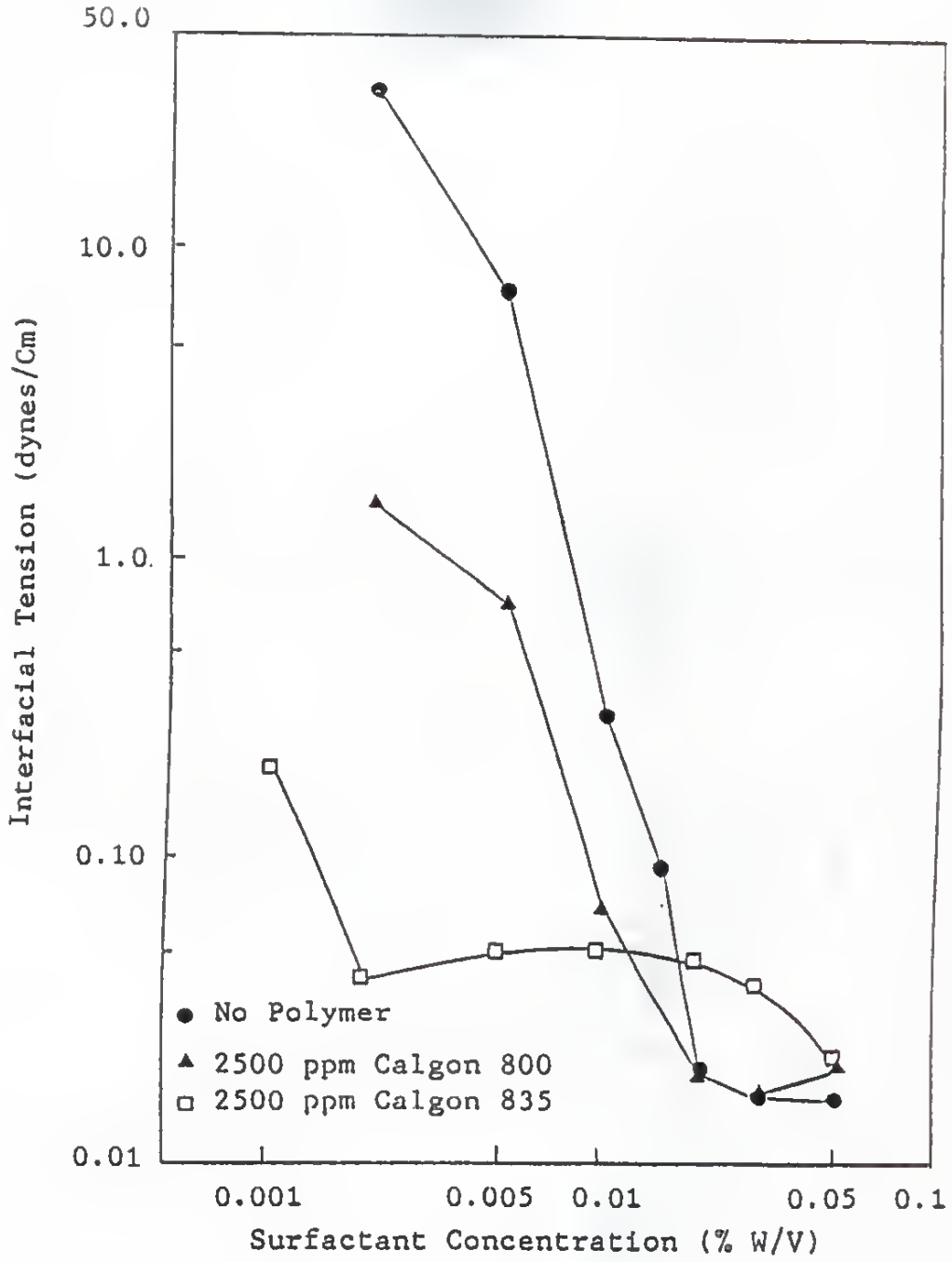


Figure 4-4. Effect of polyacryamides on the interfacial tension of TRS 10-80 surfactant solution against n-hexane. Brine (1.0% NaCl, w/v) contained TRS 10-80 and 2500 ppm polymer. WOR = 1.0. Taken from Desai, N., Ph.D. dissertation, p.35, University of Florida.

the surfactant concentration on IFT at the fixed concentration of the polymer (116).

As the concentration of the aurfactant increased, the IFT decreaaed and remained more or lesa invariant; this plateau began near the effective critical micellar concentration (cmc) of the surfactant (about 0.02%). The initial decrease in the IFT is very pronounced compared to the IFT of the aurfactant solution without the polymer. Further, it ahould be noted that more hydrolyzed polyacrylamides is more effective than the lesa hydrolyzed polyacrylamidea in lowering the IFT. The same phenomena were also observed for the different oila and surfactants as shown in Figures 4-5 and 4-6 (116).

The experimental results by Desai (116) can be summarized as followa:

1) the addition of polyacrylamides to the anionic surfactant solution lowered the IFT at a very low concentration of the surfactant,
2) the decrease in interfacial tension was most pronounced by the intial 500 to 1000 ppm of the polymer,
3) polyacryamides with a greater degree of hydrolyais were more effective than thoae with smaller degree of hydrolysia, and
4) the aame phenomena as above were obtained for various oila and anionic surfactants.

As discuased in the introduction, it ia unlikely that the anionic polymer would bind with the anionic surfactant to form the

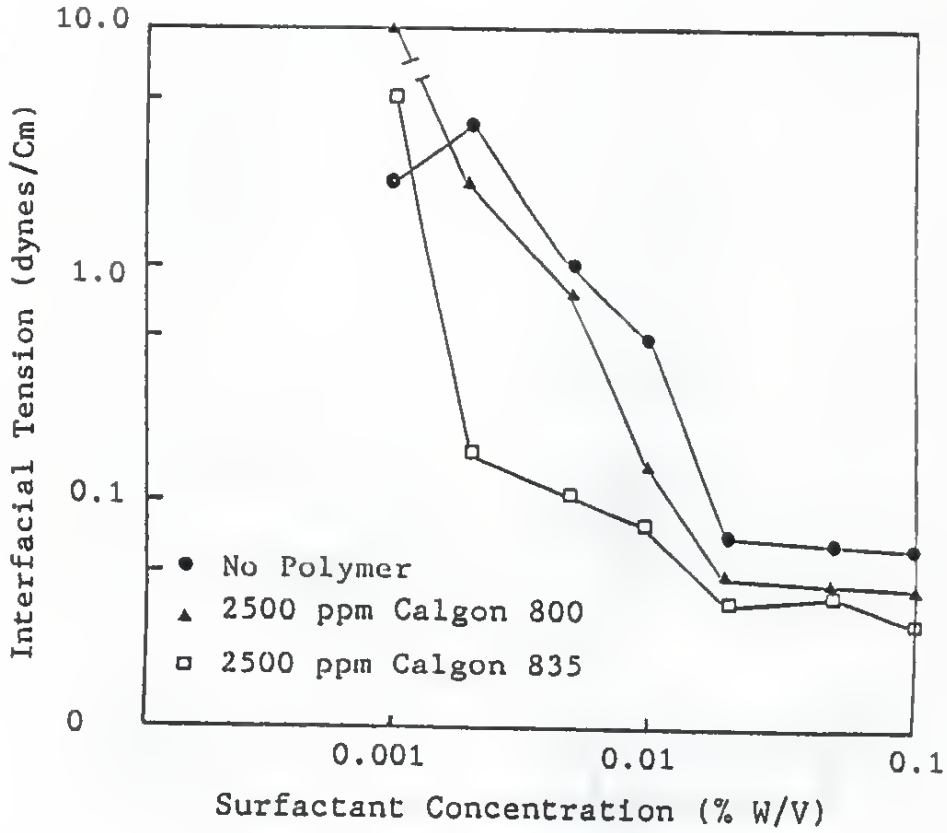


Figure 4-5. Effect of surfactant concentration on the interfacial tension of TRS10-80 system against n-dodecane. Brine (1.0 % NaCl, w/v) contained TRS10-80 (and 2500 ppm polymer). WOR = 1.0. Taken from Desai, N., Ph. D. dissertation, p.36, Univ. of Florida, 1983.

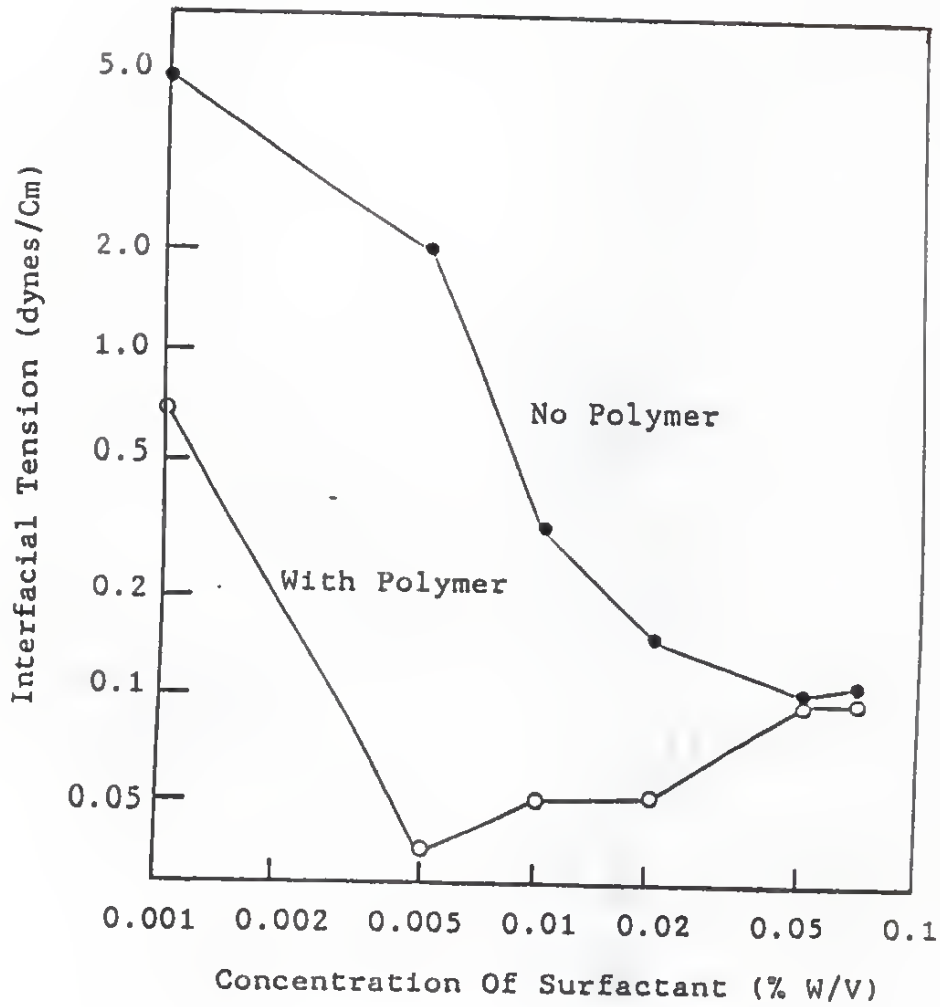


Figure 4-6. Effect of aurfactant concentration on the interfacial tension of Texaa #2 syatem against n-decane. Brine (1.0 % NaCl, w/v) contained Texas #2 (and 2500 ppm Calgon 835). WOR = 1.0. Taken from Desai, N., Ph. D. dissertation, p.40, Univ. of Florida, 1983.

complex. The electrical repulsion between the anionic polymer and the anionic surfactant will prevent forming the complex. The formation of micellea within the polymer molecules (152) is also unlikely for the same reason. Table 4-1 showa the resulta of dialysis atudiea by Desai (116). Concentration of the surfactant was kept low because it waa at low concentration that the polymer exhibited dramatic reduction in IFT. If indeed aurfactant was binding to the polymer, then the partition coefficient should be less than one. As can be seen from Table 4-1, there is no evidence of binding of surfactant by the polymer. Figure 4-7 shows the decrease in surface tension with the concentration of the surfactant at a fixed concentration of the polyacrylamide. With or without the polymer, the aurface tension decreased linearly and reached the plateau region at cmc. However, the surface tension with the polymer ia somewhat lower than that without the polymer.

The previous studies (135, 142, 146) ahowed that the surface tension decreased, then reached at the first plateau region and decreased again until the second plateau region at cmc when the complex was formed between the surfactant and the polymer (see Figure 1-12). The first plateau region was reaaoned that the complex was formed at this concentrationa of surfactant. However, no multiple plateau was formed in Figure 4-7 for anionic polymer-anionic surfactant syatem in contrast to Figure 1-12 for nonionic polymer-ionic surfactant ayatem. As mentioned earlier, this phenomenon is consistent with the previoua study for nonionic

Table 4-1. Dialysis Measurements on Solutions of Surfactanta and Polymers

Polymer: Calgon 835 (Partially hydrolyzed polyacrylamide)
Brine: 0.1 % (w/v) NaCl

Surfactant Type	Initial Concentration %w/v	Polymer Concentration (ppm)	Partition[a] Coefficient
Petroatep420	0.001	0	1.0
	0.001	300	1.1
	0.001	600	1.2
	0.001	1000	1.1
	0.001	1500	1.1
Brine: 1.0% w/v NaCl Petrostep420	0.004	2000	1.1
Texas #2(UT-2)	0.005	2000	1.0

a. $= \frac{\text{Concentration of surfactant in solvent phase (outside bag)}}{\text{Concentration of surfactant in polymer solution phase (inaide bag)}}$

b. Taken from Desai, N., "Surfactant-Polymer Interactions in Enhanced Oil Recovery System," Ph.D. Dissertation, p.53, University of Florida, 1983.

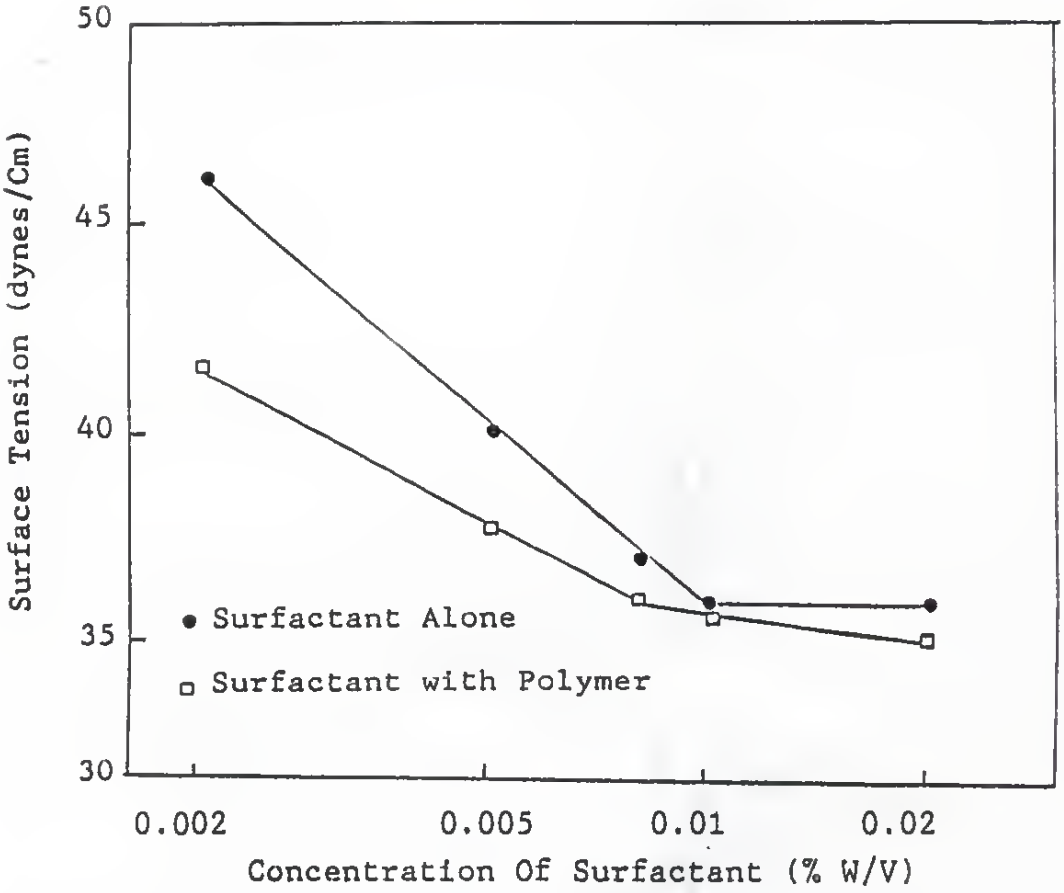


Figure 4-7. Surface tension of surfactant system containing TRS 10-80, brine (1.0% NaCl, w/v) (and 2000 ppm Calgon 800).

polymer-cationic surfactant system where no complex was formed (142).

The foregoing discussion is again supported by the data shown in Figure 4-8. The pure anionic surfactant, SDS, was used with another anionic biopolymer, xanthan, to check the change of the surface tension. However, in this case, the concentration of the surfactant was fixed and the concentration of the polymer increased. If the complex was formed in the solution, the surface tension should have increased due to the formation of the complex as the concentration of the polymer is increased (135). Therefore, it is again unlikely that the complex formation for the anionic polymer-anionic surfactant system will occur. Additional evidence that the no complex was formed between anionic polymer and anionic surfactant can be seen in Figures 4-4 and 4-5 which were taken from Desai's study (116). As mentioned before, the IFT was more effectively reduced as the polymer was more hydrolyzed. As the polymer is increasingly hydrolyzed, more electrical repulsion and increased hydrophilicity nature are expected.

4.4 The Excluded Volume Effect of Anionic Polymers

The foregoing discussion of the experimental results supports the following mechanism proposed by Desai (116) for the large reduction in the IFT of anionic surfactant solutions upon adding the anionic polymer. First, consider the dilute anionic surfactant

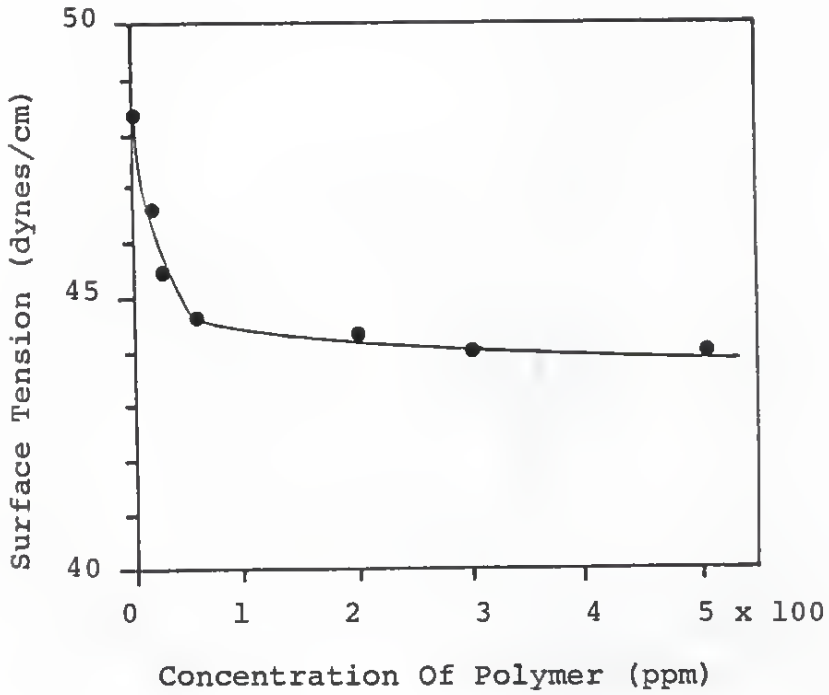


Figure 4-8. Surface tension of SDS-Xanthan 4800C system. Concentration of SDS was 2 mM.

solution alone. The anionic surfactant is all in monomeric form - some in bulk oil, some adsorbed at the oil/brine interface, but most of the surfactant is dispersed in the bulk brine as shown in Figure 4-9 (a). Since the anionic polymer molecules are highly water soluble, almost all of them are dispersed in the bulk brine upon adding them to the brine phase. However, the anionic polymer does not bind the anionic surfactant, so the volume taken up by the polymer molecules is excluded to the surfactant molecules as shown in Figure 4-9 (b). Further, with the negatively charged polymers, there is a diffuse electrical region around the polymer molecules which would be excluded to the similarly charged anionic surfactants due to electrical repulsion. Consequently, the anionic surfactant molecules would be excluded from a volume - the bulk of which is determined by the size of the anionic polymer coil, the number of the polymer molecules, and the charge density on the polymer molecules. The effective excluded volume per polymer molecule is shown as a dotted circle in Figure 4-9 (b).

The previous experimental observation agrees with the proposed mechanism: as the polymer concentration is increased, more surfactant molecules are driven away from the aqueous bulk and to the interface because the effective concentration of the surfactant in the aqueous phase increases due to the less available volume for the surfactant in the aqueous phase. This would decrease the interfacial tension until the interface is saturated by surfactant molecules as shown in Figure 4-3; as the charge density on the polymer or size of the polymer coil is increased, again more volume

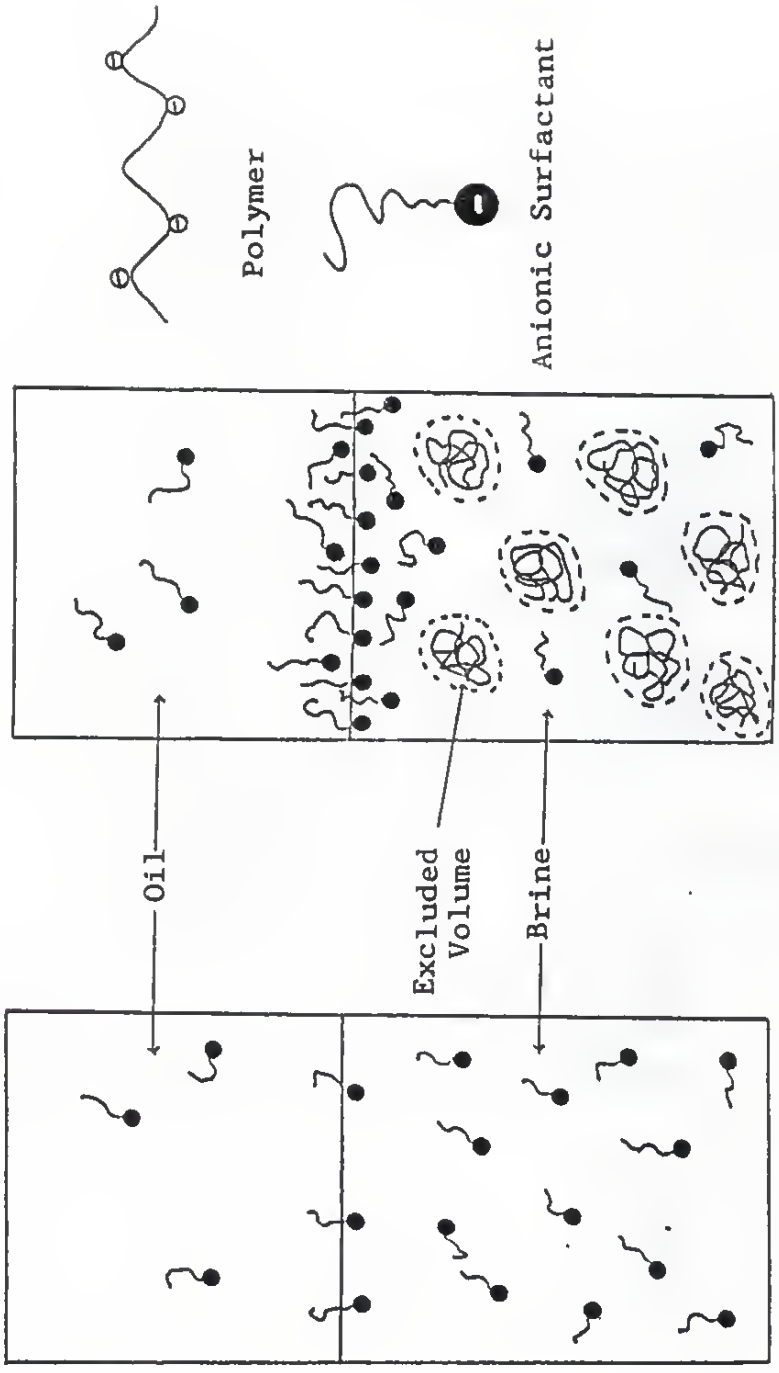


Figure 4-9. A schematic presentation of the excluded volume effect of polymer on surfactant solution: (a) in the absence of polymer; (b) in the presence of polymer.

is excluded, causing greater adsorption at the interface and therefore lower IFT as shown in Figures 4-4 and 4-5.

4.5 Effective Concentration of the Surfactant

To verify Desai's proposed mechanism (116), the effective concentration of the anionic surfactant in the presence of the anionic polymer was first calculated from the excluded volume by the polymer molecules; the excluded volume was calculated from the light scattering experiments as explained in the next few pages. The effective concentration of the anionic surfactant in the presence of the anionic polymer was defined as the anionic surfactant concentration based on the volume obtained by subtracting the unavailable volume for the surfactant from the total volume of the solution. The IFT at a given surfactant concentration in the presence of the polymer was obtained from the IFT data for the surfactant solution alone (without the polymer) using the calculated effective concentration of the surfactant.

When the polymer molecule is assumed to be a sphere, the excluded volume per polymer molecule (U_{pp}) in the aqueous polymer solution without a surfactant is expressed as (229)

$$U_{pp} = (4/3)\,\pi\,[2\,(R_p + R_{pe})]^3 \qquad (4\text{-}3)$$

where R_p is the radius of the polymer molecule and R_{pe} results from the exclusion forces such as electrical repulsion. The excluded

volume (U_{pp}) is then related to the second virial coefficient (B) through the equation (229):

$$B = (L / 2) (U_{pp} / M^2). \qquad (4-4)$$

where L and M are reapectively Avogardro's number and molecular weight of the polymer. Since B and M can be obtained from the SLS experiments as mentioned earlier, only unknown U_{pp} can be calculated. While U_{pp} ia the excluded volume due to polymer moleculea, the necessary excluded volume we are concerned with in this atudy is the excluded volume (U_{sp}) between the aurfactant molecules and the polymer molecule. U_{ap} may be written aa

$$U_{sp} = (4 / 3)\pi [(R_p + R'_{pe}) + (R_a + R'_{se})]^3 \qquad (4-5)$$

where R_a is the radius of the surfactant, and R'_{pe} and R'_{se} result from the exclusion forces for a polymer molecule and a surfactant molecule. Obviously, R_a, R'_{pe}, and R'_{se} cannot be calculated. However, by assuming $R_e = R'_{pe} + R'_{se}$ and neglecting R_s because $R'_{pe} >> R'_{se}$ and $R_p >> R_a$, $U_{sp} = (4 / 3)\pi (R_p + R_{pe})^3$ and $U_{sp} = U_{pp} / 8$. Consequently, the excluded volume, U_{sp}, can be estimated from the meaaurement of the aecond virial coefficient using the SLS technique for a polymer solution without a aurfactant.

Figure 4-10 shows the experimental resulta uaing Calgon 800. It should be mentioned that Calgon 800 waa chosen becauae the line waa straight up to a high concentration of polymer, indicating that

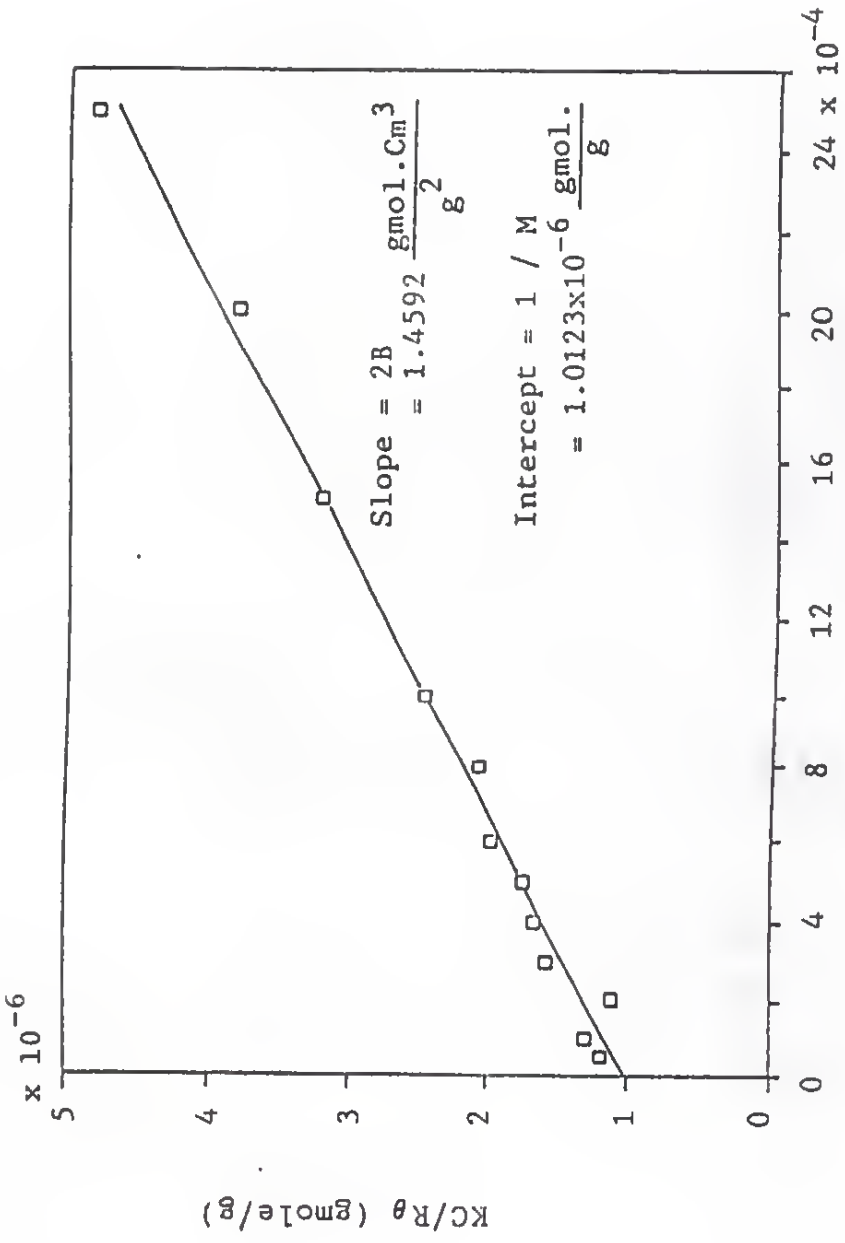


Figure 4-10. Result of light scattering experiment for polymer in brine (1.0% NaCl, w/v). Polymer was Calgon 800.

interaction terms higher than binary interaction were not significant at the concentration at which this study was done (2500 ppm). In contrast, as shown in Figure 4-11, the more hydrolyzed polymer produced a curved line. This indicated that significant interactions higher than the binary interaction existed in this polymer solution. Therefore, it could produce the incorrect excluded volume at the chosen high concentration of the polymer (2500 ppm). From the intercept and the slope of Figure 4-10, the molecular weight and the second virial coefficient were 0.0879×10^{6} g/gmol and 7.29577×10^{-4} gmol cm^3 / g^2, respectively. The excluded volume (U_{sp}) calculated from the second virial coefficient was 2.957×10^{-16} ml / polymer molecule. In comparison, the effective diameter of the polymer was obtained from the diffusion coefficient using QELS technique. It should be noted that the effective diameter (similar to the physical dimension of the polymer molecule) does not consider the exclusion forces, so that the excluded volume (U_D) calculated based on the effective diameter should be less than the excluded volume, U_{sp}. The effective diameters depending on the concentration of the polymer are shown in Figure 4-12. It was found that U_{sp} and U_D were 826 Å and 523 Å at 2500 ppm of the polymer.

Tables 4-2 and 4-3 and Figures 4-13 and 4-14 show the comparison between the experimental values and the calculated values of interfacial and surface tension based on U_{sp} and U_D. At 2500 ppm of the polymer, the excluded volume by the polymer molecules were 45.1% and 11.3% of total volume of the solution on the basis of U_{sp}

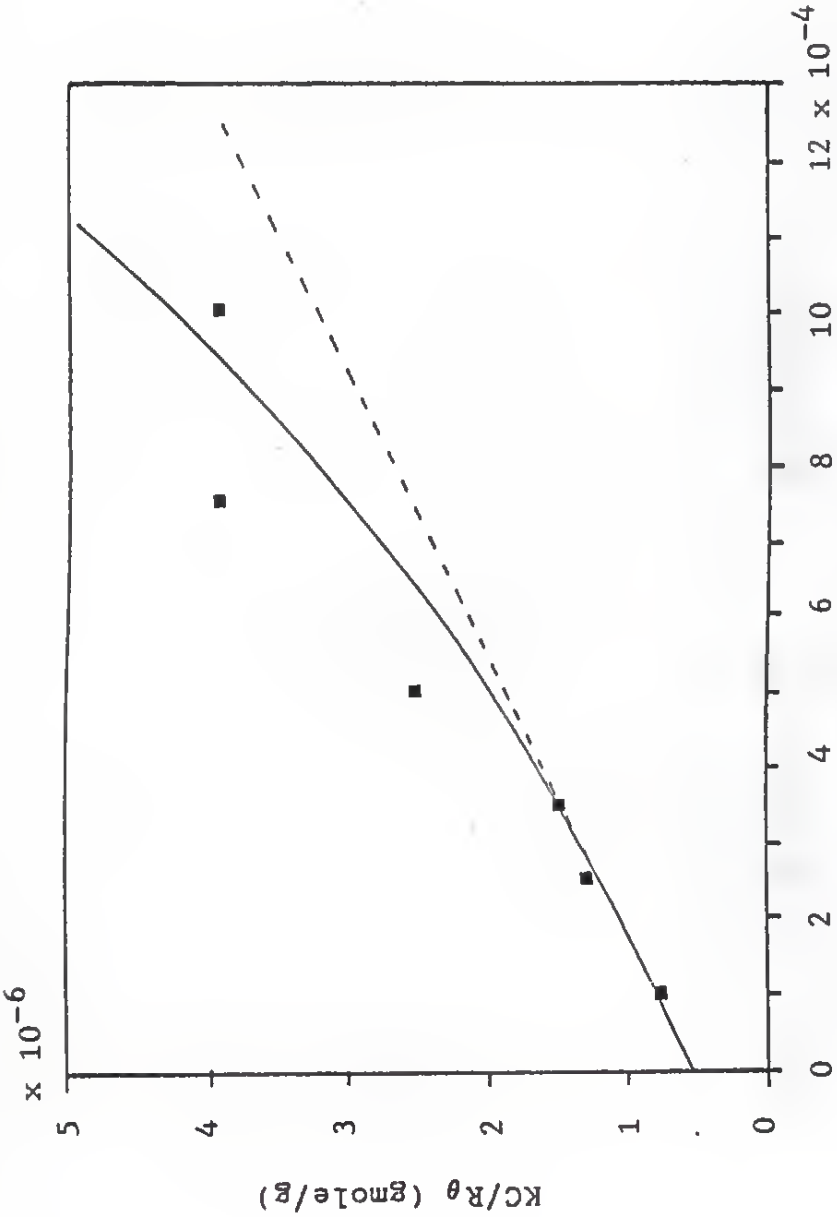


Figure 4-11. Result of light scattering experiment for polymer in brine (1.0 % NaCl, w/v). Polymer = Calgon 825.

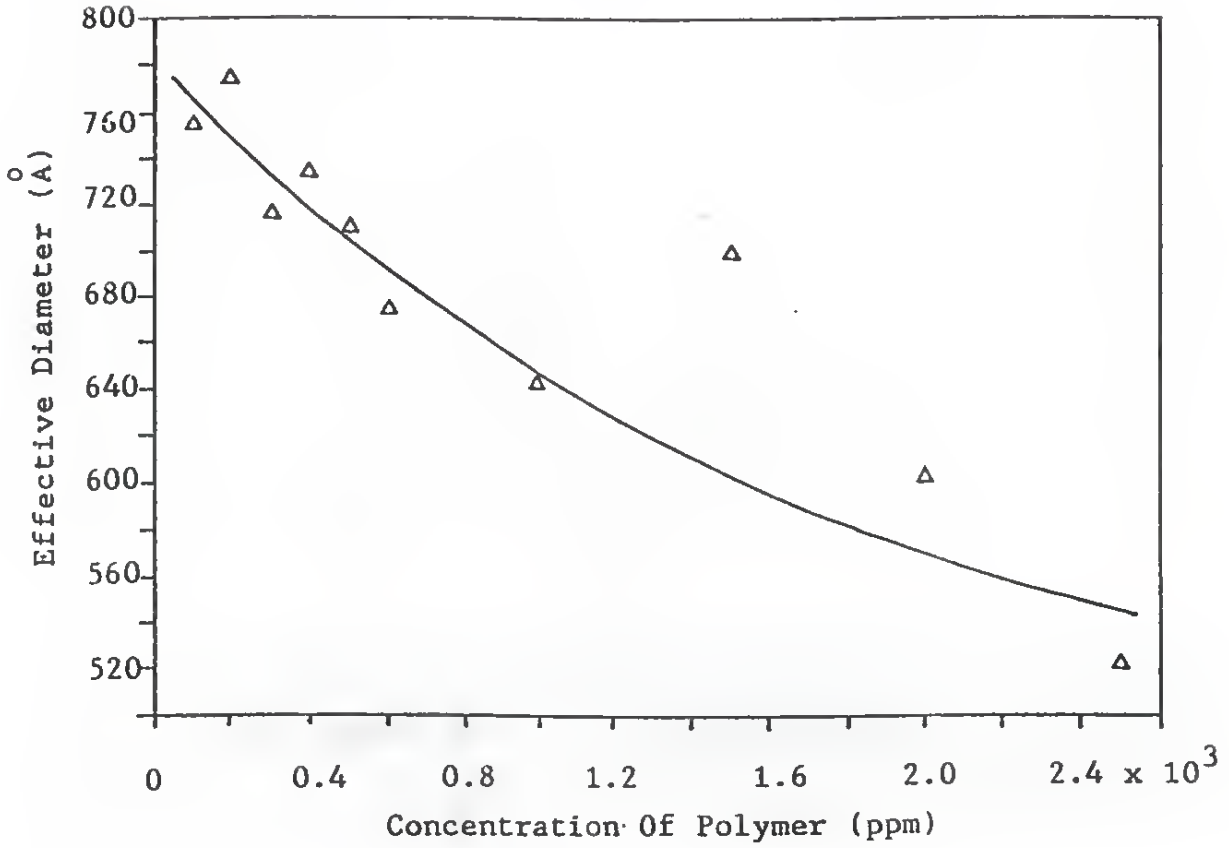


Figure 4-12. Effective diameters of polymer molecules depending on the concentration of polymer in brine (1.0 % NaCl, w/v). Polymer = Calgon 800.

Table 4-2. Experimental and Calculated Values of Effective Concentration and Interfacial Tension

Concentration of Surfactant (%, w/v)	Effective[a] Concentration (%, w/v)		IFT with Polymer[a]			IFT of Surfactant Solution
			Experimental	Calculated		
	U_{sp}	U_D		U_{sp}	U_D	
0.001	0.0018	0.0013	16	3.67	2.85	2.35
0.002	0.0036	0.0023	2.3	1.90	3.70	4.00
0.005	0.0091	0.0056	0.705	0.59	0.94	1.00
0.01	0.0182	0.0113	0.103	0.11	0.44	0.50
0.02	0.0364	0.0226	0.044	0.066	0.069	0.07
0.05	0.0911	0.0564	0.042	0.055	0.062	0.063
0.1	0.1820	0.1129	0.040	0.053	0.053	0.053

a. U_{sp} and U_D are the unavailable volume for surfactant moleculea calculated on the basis of the excluded volume and effective diameter of polymer molecule, reapectively. This table represents the values of effective concentration and interfacial tension calculated on the basia of U_{sp} and U_D. IFT is expressed as dynes/cm; interfacial tenaion of TRS 10-80 ayatem againat n-dodecane (brine contained 1.0% NaCl and TRS 10-80 and/or 2500ppm polymer).

Table 4-3. Experimental and Calculated Values of Effective Concentration and Surface Tension

Concentration of Surfactant (%, w/v)	Effective[a] Concentration (%, w/v)		ST with Polymer[a]			ST of Surfactant Solution
			Experimental	Calculated		
	U_{sp}	U_D		U_{sp}	U_D	
0.002	0.0031	0.0022	41.6	43.0	45.6	46
0.005	0.0078	0.0055	37.8	37.6	39.5	40
0.008	0.0125	0.0088	36.1	36.1	36.7	37.1
0.01	0.0156	0.0110	35.7	36.1	36.1	36.1
0.02	0.0313	0.0220	35.2	36.1	36.1	36.1

a. U_{sp} and U_D are the unavailable volume for surfactant molecules calculated on the basis of the excluded volume and effective diameter of polymer molecule, respectively. This table represents the values of effective concentration and surface tension (ST) calculated on the basis of U_{sp} and U_D. Surface tension is expressed as dynes/cm; the system contained 1.0% NaCl and TRS 10-80 and/or 2000ppm polymer.

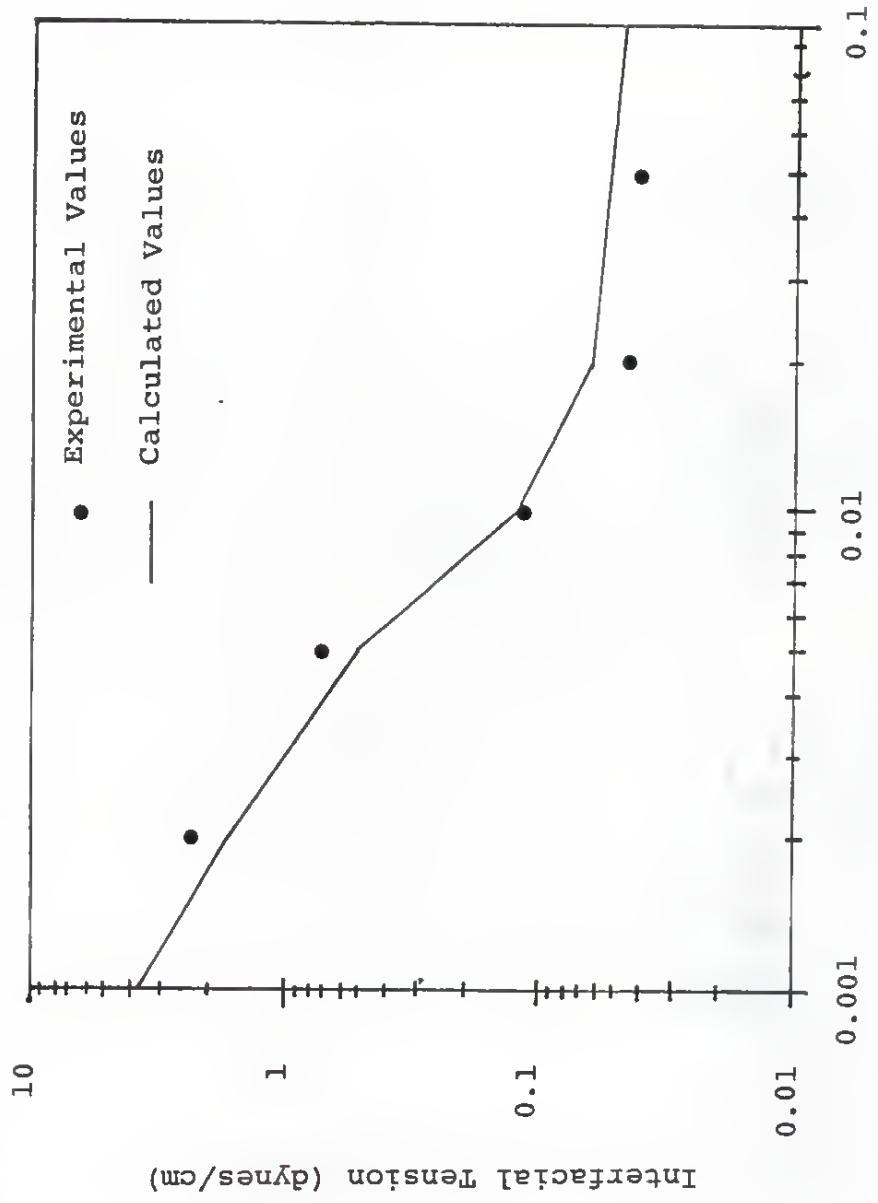


Figure 4-13. Experimental and calculated values of interfacial tension. Calculated values of interfacial tension were obtained using effective concentratration of surfactant from excluded volume of polymer molecules. System contained brine (1.0% NaCl, w/v) and n-dodecane. Brine contained TRS 10-80 and 2500 ppm polymer. WOR = 1.0.

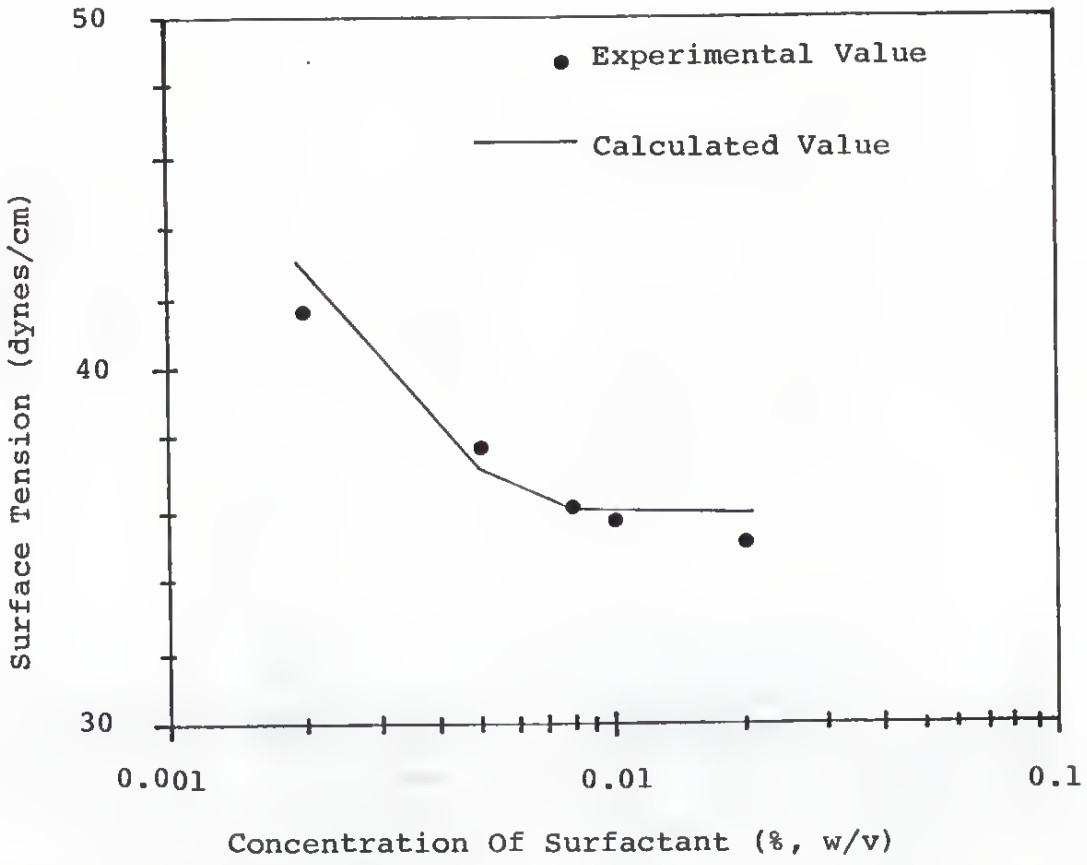


Figure 4-14. Experimental and calculated values of surface tension. Calculated values were obtained using effective concentration of surfactant from excluded volume of polymer molecules. System contained TRS 10-80, brine (1.0% NaCl, w/v) and 2000 ppm Calgon 800.

and U_D, respectively. When U_{sp} was used, the calculated values were reasonably well matched with the experimental values. This again implies that the excluded volume is not only the volume occupied by the polymer but also the volume unavailable to the surfactant due to exclusion forces such as electrical repulsion.

It should be noted that an additional mechanism may be involved in some anionic polymer-anionic surfactant systems. While the excluded volume effect by polymer molecules well predicts the shift of interfacial tension by the effective concentration of the surfactant which is greater than the actual concentration, this mechanism cannot explain lowering of interfacial tension below the value of interfacial tension at cmc as shown in Figure 4-6.

4.6 Oil Displacement Efficiency

The excluded volume effect by the polymer on the surfactant in the aqueous solution can have a great impact in several applications employing anionic polymer-anionic surfactant systems. For example, in the enhanced oil recovery, the modified polymer flooding using the polymer solution with a small amount of the surfactant can combine the effect of polymer flooding and surfactant flooding because of its ability to produce the low interfacial tension as well as the high sweep efficiency. The polymer flooding enhances the oil recovery by increasing the sweep efficiency due to the high viscosity (230). However, it cannot reduce the interfacial tension so that all the oil contacted by the polymer solution cannot be recovered. In contrast, surfactant-polymer flooding enhances oil

recovery by reducing the interfacial tension and increasing aweep efficiency (78). However, a high concentration of the surfactant (5-20%) results in increased cost so that surfactant flooding ia not economical at the current low price of oil. Therefore, modified polymer flooding can be economical, with enhanced oil displacement, because the required amount of the aurfactant is so amall (-0.02%) that it will not greatly increase the cost when compared to the polymer flooding.

Figurea 4-15 and 4-16 show the schematic of oil recovery experiments and their resulta. As expected, modified polymer flooding most effectively displaced residual oil (75%) when compared to polymer flooding (33%) and flooding with surfactant alone (15%). Since the viscoaity was not expected to change much with the addition of a amall amount of surfactant, the decrease in the IFT due to the excluded volume effect enhanced oil displacement by 42% compared to polymer flooding. The poor oil displacement by the surfactant aolution alone reaulted basically from poor mobility control (117, 231).

4.7 Conclusions

The dramatic reduction in the IFT of a very dilute anionic surfactant solution in the presence of anionic polymer was cloaely examined. Anionic surfactanta used were commercial petroleum sulfonate and pure aurfactant (SDS) while the used anionic polymers were polyacrylamides with different degrees of hydrolysis and

Flow ⟶

				Tertiary Oil Recovery
2500 ppm Polymer Solution With 0.02% TRS10-80	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	75 %
Modified Polymer Flooding with a Small Amount Of Surfactant				
2500 ppm Polymer Solution	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	33 %
Polymer Flooding				
0.02% TRS10-80 Solution	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	15 %
Flooding With Surfactant Solution				

Figure 4-15. A schematic presentation of oil displacement experiments.

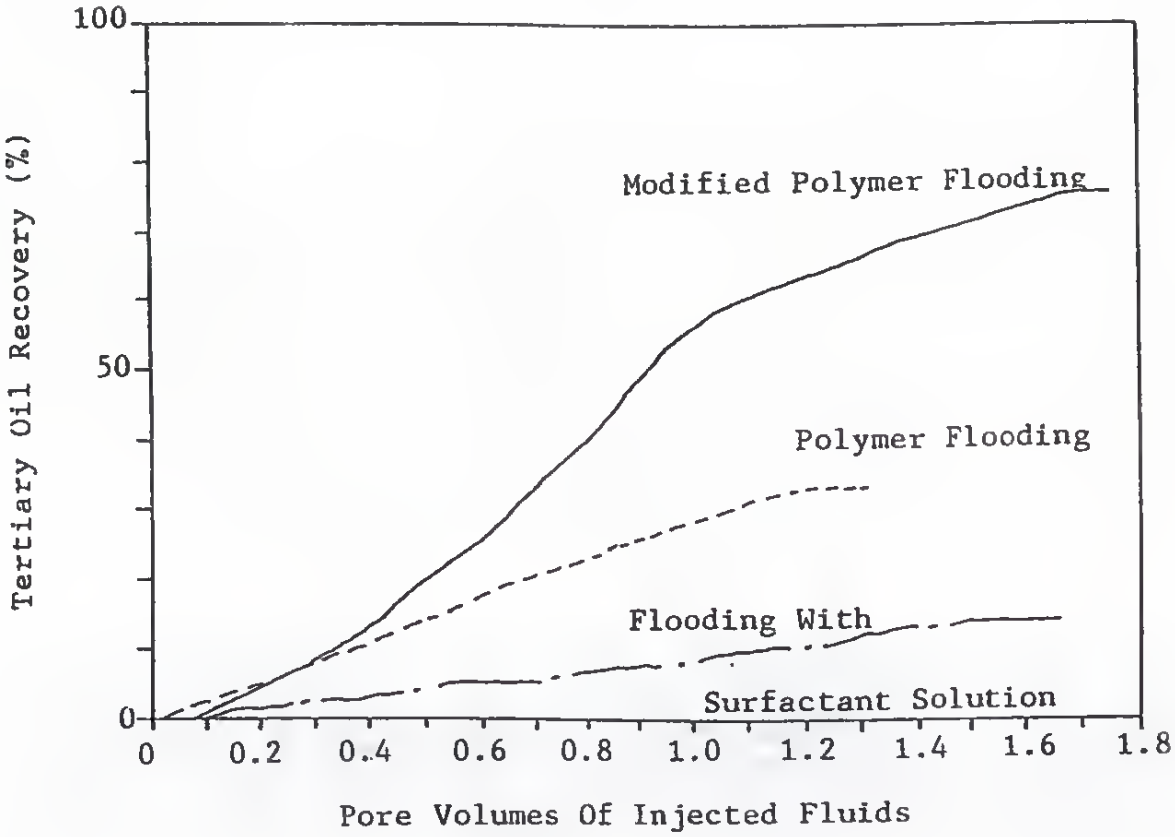


Figure 4-16. Oil production history. Slug compositions can be found in Figure 4-15.

biopolymer (high-pyruvate xanthan). The conclusiona from this study can be summarized as followa:

1. Both the commercial and pure anionic aurfactants in this study were effective in the reduction of IFT or aurface tension in the preaence of the anionic polymer, polyacrylamides or biopolymer.
2. The anionic polymera by themselves did not exhibit surface activity.
3. Surface tension data for the anionic polymer-anionic surfactant system indicated the no formation of complex between the aurfactant and polymer.
4. The excluded volume effect by the polymer on the aurfactant was calculated to verify the Desai's proposed mechanism for anionic polymer-anionic aurfactant aystems using light scattering techniquea.
5. The resulta frome light scattering experiments showed that the excluded volume ia not only the volume occupied by polymer molecules but alao the volume unavailable to the surfactant moleculea due to exclusion forces such as electrical repulsion between surfactant and polymer molecule.
6. The excluded volume was experimentally obtained using SLS technique and the effective concentration of the aurfactant in the preaence of the polymer was calculated. The experimental values of IFT and the calculated values of IFT uaing the effective concentration were in good agreement.

7. Oil displacement efficiency was greatly improved by adding a small amount (0.02%, w/v) of anionic surfactant into the anionic polymer solution, in comparison to the anionic polymer alone (75% vs. 33%).

CHAPTER 5

THERMAL CONDUCTIVITY OF MICROEMULSIONS

5.1 Introduction

Heat transfer is very important in chemical and energy-related industries. Petroleum oils (232), diphenyl/diphenyl oxide eutectic (233, 234), and molten salts (235) are the well-known heat transfer media, which become liquid at the operating temperature. To estimate heat transfer rate using such a liquid medium, it is necessary to know the thermal conductivity of the liquid. Even though a number of equations to estimate the liquid mixture thermal conductivity have been proposed (156, 166-170), many of the equations are applicable only to binary systems and it is still unclear whether these equations can be applied to the multicomponent mixtures (17), indicating that the development of a complete theoretical model is very difficult.

Considering that energy is primarily exchanged by oscillations of molecules in the shared force field surrounding each molecule in a liquid, it is interesting to see the effect of the structure of liquid on thermal properties. Therefore, the effect of the structure of liquid on thermal diffusivity was studied by comparing an isotropic liquid to a birefringent liquid using the simple transient method developed in our laboratory. From thermal

diffusivity, density and heat capacity values of a liquid sample, thermal conductivity can be calculated. This study was further extended to thermal conductivity of microemulsions because of the unique microstructure of microemulsions (15) and their potential use in practical applications such as cutting fluid (236) and as a possible heat transfer medium. Finally, the experimental values of thermal conductivities of microemulsions were compared to the values obtained from the known equations for liquid mixtures and macroemulsions.

5.2 Theoretical Model for the Measurement of the Thermal Conductivity of Liquids

Consider a spherical ball which has a uniform temperature (T_o) at time, $t = 0$. At $t > 0$, the sphere is immersed into the liquid which has a uniform temperature (T_1). The temperature distribution as a function of time and position can be obtained by solving the following equation with the boundary and the initial conditions assuming that heat transfer occurs only by conduction and that only radial direction (r) is considered:

$$(1 / r) (\delta^2 (r T) / \delta r^2)) = (1 / \alpha) (\delta T / \delta t) \quad (5\text{-}1)$$

$$T (r, 0) = T_o \qquad 0 < r < R \qquad (5\text{-}2)$$

$$T (R, t) = T_1 \qquad t > 0 \qquad (5\text{-}3)$$

where α is thermal diffusivity defined as $K / \rho C_p$ (K = thermal conductivity, ρ = density, and C_p = heat capacity). The above

equation can be solved without any difficulty uaing the separation of variables method (237). The detailed procedure for the solution is described in the Appendix. The resulting solution is:

$$\frac{T - T_1}{T_0 - T_1} = -(2R/\pi)(1/r) \sum_{n=1}^{\infty} (-1)^n (1/n) \mathrm{SIN}(n\pi r/R) \times \mathrm{EXP}(-(n\pi/R)^2 \alpha t) \qquad (5\text{-}4)$$

The solution ia then reduced for the temperature at the center of the sphere as follows:

$$\left.\frac{T - T_1}{T_0 - T_1}\right|_{r=0} = -2 \sum_{n=1}^{\infty} (-1)^n \mathrm{EXP}(-(n\pi/R)^2 \alpha t) \qquad (5\text{-}5)$$

The detailed procedure is again described in the Appendix. When t is large, the terms higher than the firat term in the equation 5-5 will be negligible, resulting in:

$$\left.\frac{T - T_1}{T_0 - T_1}\right|_{r=0,\ t\to\infty} = 2\ \mathrm{EXP}\ (-(\pi^2 \alpha/R^2)\ t) \qquad (5\text{-}6)$$

By taking the logarithm for both aidea,

$$\ln \left.\frac{T - T_1}{T_0 - T_1}\right|_{r=0,\ t\to\infty} = -(\pi^2 \alpha/R^2)t + \ln 2 \qquad (5\text{-}7)$$

From the equation 5-7, $\ln [(T - T_1) / (T - T_1)]_{r = 0,\ t\to\infty}$ is a linear function of time (t), having $(-\pi^2 \alpha / R^2)$ and ln 2 as a slope

and an intercept, respectively. Therefore, at a large t, α can be obtained from the slope of the straight line on the semi-log plot of $[(T - T_1) / (T_o - T_1)]_{r = 0}$ vs. t aa ahown in Figure 5-1.

Now, consider the liquid in a spherical bottle as shown in Figure 5-2. Since the area of the cylindrical arm attached to the spherical bottle is small compared to the area of the aphere, it may be considered as a perfect sphere. Further, the thickness of the wall of the spherical bottle is so small that the temperatures at the inside and outside of the wall may be asaumed to be the same as the temperature of the heating water, T_1. Obviously, the initial temperature gradient ($\Delta T = T_1 - T_o$) ia large, resulting in both conductive and convective heat transfer. However, as $t \to \infty$, T becomes so small that the convective heat transfer may be considered negligible. At this stage, the linear relationship between $\ln [(T - T_1) / (T_o - T_1)]_{r = 0}$ and t is obtained with a different intercept from ln 2 depending on the liquid sample because of the convective heat transfer initially involved when ΔT is large. Therefore, thermal diffuaivity (α) can be obtained from the slope at a large t becauae the radiua of the sphere (R) is known.

5.3 Materiala and Methoda

TRS10-80 (238), AOT, Arlacel 20 were the same chemicala used in Chapter 2 for the study of alcohol-free w/o microemulsiona. Benzene was from Chemical Sample Co. and aniline waa from J. T. Baker Chemical Co. Benzene was 99.5% pure and aniline was analyzed

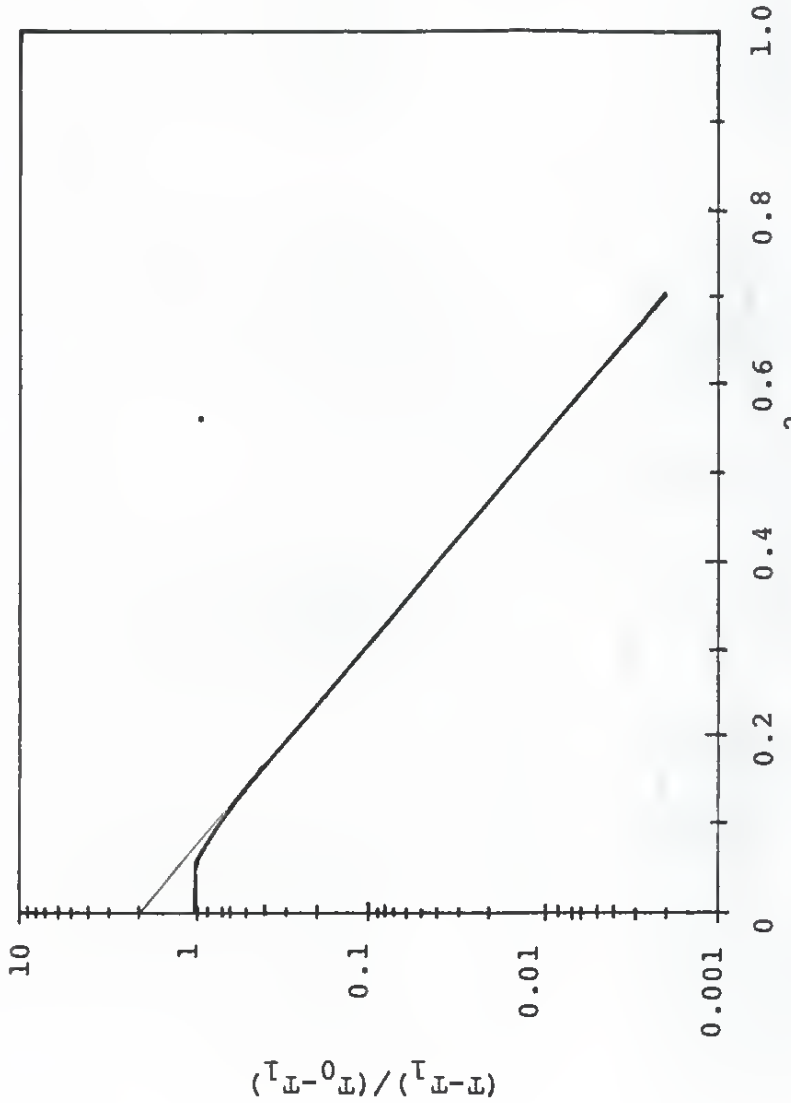


Figure 5-1. Change of temperature at the center of a sphere as a function of time. The slope of the straight line represents the value of $\pi^2\alpha/R^2$.

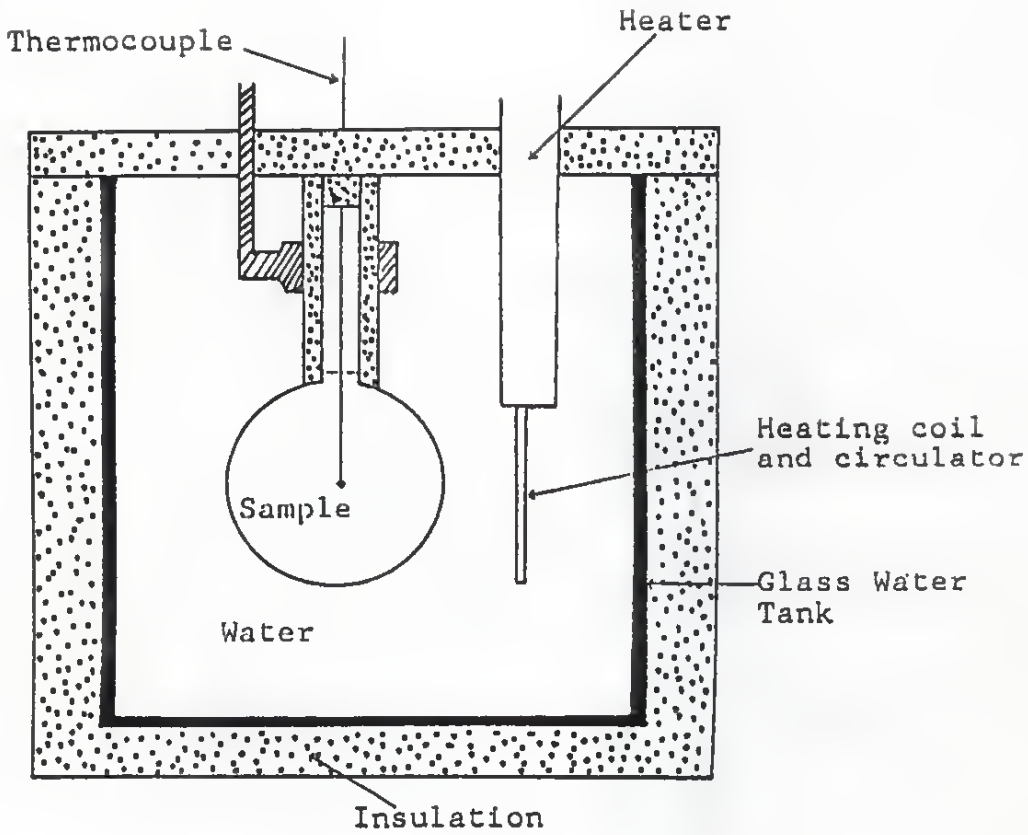


Figure 5-2. A schematic diagram of the apparatus for the measurement of the thermal diffusivity of a liquid.

reagent grade. Isobutanol (IBA) and sodium chloride were certified grades from Fisher Scientific Company. De-ionized, distilled water was used throughout this study.

A cross-section of the experimental apparatus for the measurement of thermal diffusivity is shown in Figure 5-2. A spherical flask was used as a sample container. The spherical flask was 6.35 cm in inside diameter and less than 1 mm in wall thickness. The Aamount of the liquid sample was about 1 liter. The sample bottle containing the sample was first placed in a constant temperature bath at 30 ℃ until the temperature at the center did not change as a function of time. After thermal equilibrium was reached at 30 ℃, the sample flask was immersed into a constant temperature bath which was maintained at 40 ℃ during the experiment, using a Haake E51 immersion circulating heater with a temperature controller. With a good insulation, the temperature was maintained within ± 0.01 ℃.

The temperatures at the center of the flask were recorded as a function of time. The temperature was measured using 8502-20 Centigrade Thermometer with YSI Series 700 thermoprobe from Cole Parmer, with an accuracy of 0.01 ℃. Beside the temperature at the center of the sample in the flask, the temperatures of heating water in the bath and of the flask surface were checked periodically.

It was practically difficult to locate the exact center of the sphere. However, the problem from the off-center could be overcome by using a correction factor which could be determined experimentally. Figure 5-3 shows the solution of the equation 5-1

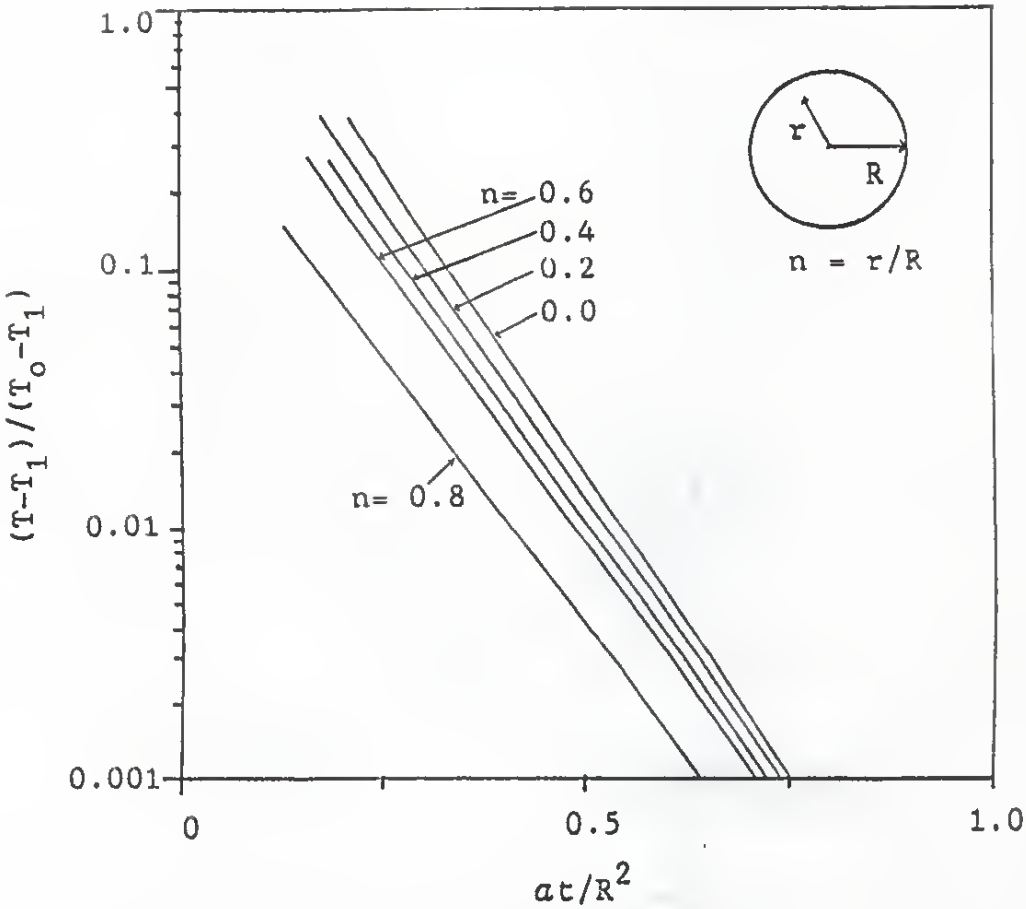


Figure 5-3. Effect of off-center on the change of temperature as a function of time.

(154). It can be seen thst a chsnge in the position of the tempersture probe from the center of the sphere to s point swsy from the center would result only in s different slope. Therefore, the problem of off-center can be corrected by a correction fsctor as long as the same locstion in the sphere is used for the messurements of the tempersture throughout the experiments. The problem of a non-perfect sphere could be slso overcome in the same wsy. Figure 5-4 shows the solutions for the different shapes indicating thst the shspe sffects only the slope (239). Figure 5-5 shows the experimental results for wster as sn example. As expected, at t larger thsn 2200 seconds, the plot becsme linear. Three experiments were done for wster snd the results sre shown in Table 5-1. The experimental values were about 10% larger thsn vslues reported in the literature (5.901×10^{-3} ft^2/hr) (154).

The experimentsl error could result from:

1) off-center position of the probe,
2) deviation from sphericsl shspe,
3) rsdisnt snd convective hest trsnsfer, snd
4) finite thickness snd different thermal diffusivity for glass wall of the sphere from thst for hesting wster.

Since the temperature grsdient for the linesr region was less than 0.1°C, it wss likely thst the lsrger experimental values for water resulted from the non-perfect sphere snd the off-center location. As shown in Figure 5-3 and 5-4, as the position becomes further away from the center snd the shspe devistes from sphere, the slope increases resulting in s higher experimental vslue of thermal

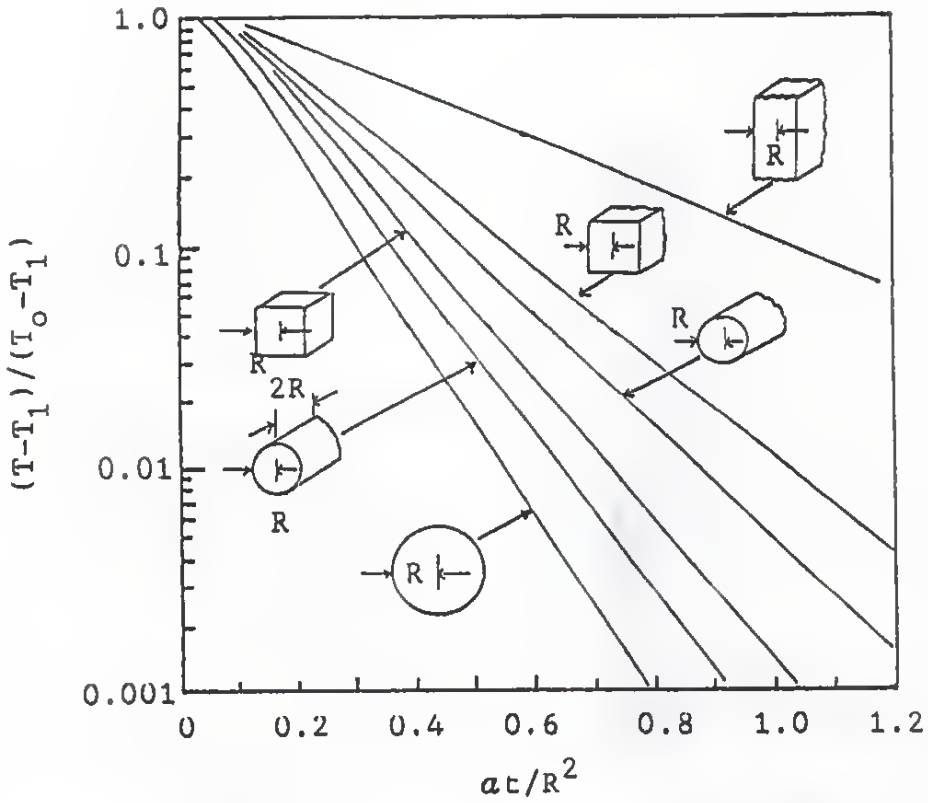


Figure 5-4. Effect of shape on the change of temperature as a function of time.

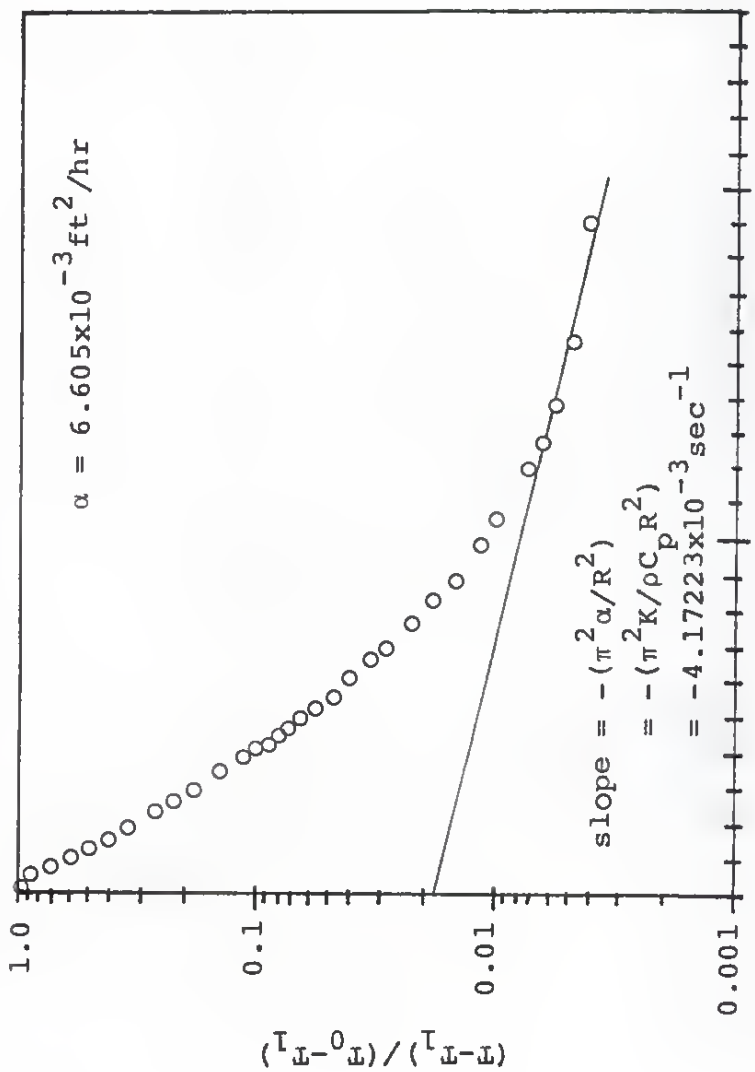


Figure 5-5. The change of temperature at the center for water.

Table 5-1. Experimental Values of Thermal Diffusivity of Water at 40 °C Using the Transient Method Developed in This Study to Find Correction Factor

Run	Experimental Value (ft^2 / hr)	Literature Value (ft^2 / hr)	Error (%)
1	6.426×10^{-3}	5.901×10^{-3}	+ 9.5
2	6.605×10^{-3}		+ 11.9
3	6.434×10^{-3}		+ 9.0
average	6.500×10^{-3}		

diffusivity than that predicted for an idealized experimental set-up. Therefore, a correction factor was obtained by comparing the average experimental value of water to the literature value. The obtained correction factor was 0.908 which was multiplied by the experimental value. Several liquids whose thermal diffusivities at 40 °C were known were used to check the validity of the apparatus. Table 5-2 represents the results. Except for ethanol, the experimental values were within 10% of values reported in the literature, which was the recommended precision by ASTM (240).

The heat capacity of the sample was measured using a Perkin-Elmer Differential Scanning Calorimeter (DSC-7) (241) and the data were analyzed by Thermal Analysis Software 7 using a 7500 Professional Computer. The temperature was increased from 34 °C to 58 °C in increments of 5 °C/min. The amount of the sample was about 0.05 g. The heat capacity was calculated from the measured heat flows of the blank, the sample and the standard using the following equations:

$$F_i = C_{p,std} \, (dT/dt) \, (m_i - m_{blk}) \qquad (5\text{-}8)$$

$$Y_i = Y'_i - F_i \qquad (5\text{-}9)$$

$$C_{p,smpl} = (Y_{std}/Y_{smpl}) \, (m_{std}/m_{smpl}) \, C_{p,std} \qquad (5\text{-}10)$$

where F_i = correction factor

dT/dt = heating rate (5 °C/min)

m_i = masses of standard or sample (g)

m_{blk} = mass of blank = mass of pan plus lid (g)

Table 5-2. Experimental Values of Thermal Diffusivity of Liquid at 40 °C

Liquid	Experimental Value x 1000 (ft^2 / hr)		Literature Value (ft^2 / hr)	Error (%)
	Before[a]	After[b]		
N-butanol	3.274 3.591	2.973 3.261	3.228×10^{-3}	- 7.9 + 3.3
Aniline	3.154 3.274	2.864 2.973	3.234×10^{-3}	- 11.4 - 8.1
Benzene	3.771 3.634	3.424 3.300	3.583×10^{-3}	- 4.8 - 8.0
Ethanol	3.333	3.026	3.425×10^{-3}	- 11.7

a. Experimental values before correction.

b. Values after correction using the correction factor, 0.908.

Y_i = heat flows of standard or sample (mW)

$C_{p,std}$ = heat capacity of standard (0.118 cal/gK)

$C_{p,ampl}$ = heat capacity of sample (cal/gK)

subscript, i, = smpl for sample and std for standard.

The heat capacity at 40 °C was obtained by interpolation from the heat capacity data between 34 to 58 °C.

The denaity of the sample was measured at 40 °C using the density bottle (241).

5.4 Effect of the Microstructure of the Liquid

Two aqueous solutions were prepared by adding TRS10-80 (5 wt.%) and isobutanol (3 wt.%) to brine solutions at two different concentrationa of NaCl 0.5 and 1.5 wt.% NaCl. The aqueous solution with 0.5 wt.% NaCl was isotropic while the aqueous solution with 1.5 wt.% NaCl was birefringent, indicating that two aqueous solutions had the strikingly different microatructures. These different microstructurea were studied by freeze-fractured electron microscope in a previoua atudy (101). The birefringence was checked using the polarizing platea at the room temperature and 40 °C.

Table 5-3 and Figure 5-6 show the experimental results of thermal diffusivitiea of the two aqueoua aolutiona at 40 °C. Thermal diffuaivities of the iaotropic and the birefringent solutions were 5.031×10^{-3} and 4.186×10^{-3} ft^2/hr at 40 °C. The difference in thermal diffusivity waa 20% when the two aqueous solutions were

Table 5-3. Thermal Diffusivity of Isotropic and Birefringent Liquids at 40 °C

Liquid	Thermal Diffusivity (ft^2 / hr)	Average (ft^2 / hr)	Deviation (%)
Water	5.901×10^{-3}		
Isotropic Liquid[a]	5.118×10^{-3}		+ 1.7
	5.246×10^{-3}	5.031×10^{-3}	+ 4.3
	4.730×10^{-3}		- 6.0
Birefringent Liquid[b]	4.118×10^{-3}	4.186×10^{-3}	- 1.6
	4.254×10^{-3}		+ 1.6

a. 5 wt.% TRS10-80, 3 wt.% isobutanol, and 0.5 wt.% NaCl in water.

b. 5 wt.% TRS10-80, 3 wt.% isobutanol, and 1.5 wt.% Nacl in water.

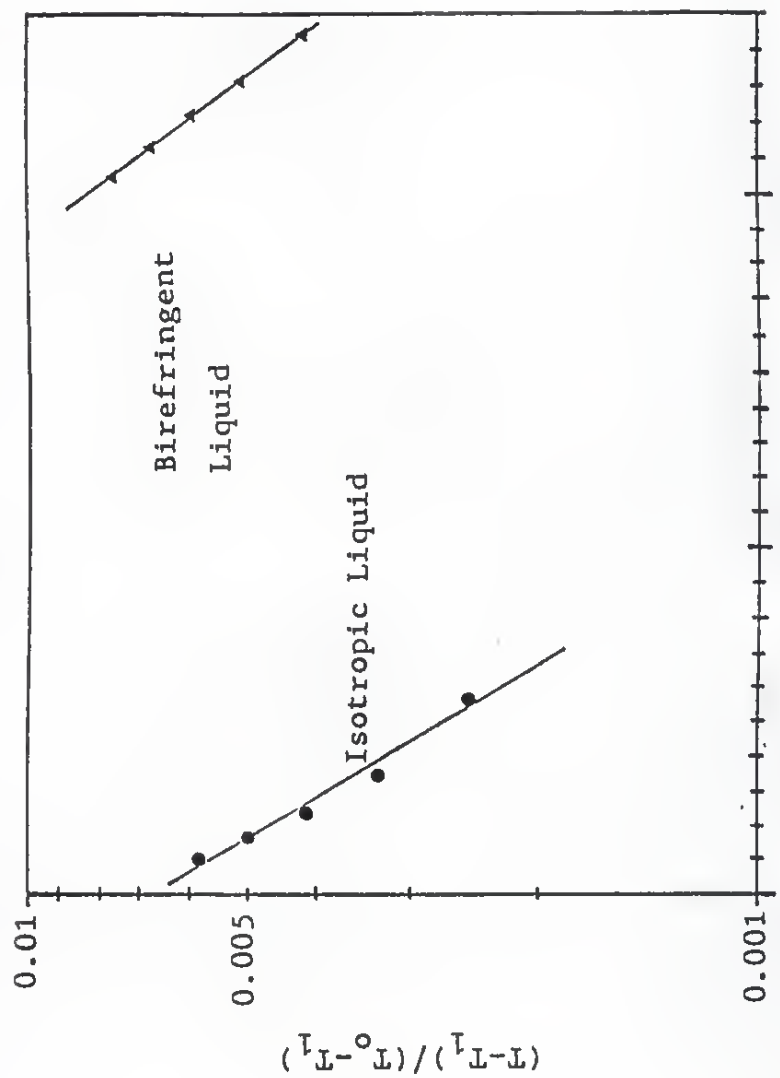


Figure 5-6. The change of temperature at the center for isotropic and birefringent liquid. TRS 10-80 (5 wt.%), isobutanol (3 wt. %) and brine (0.5 wt.% NaCl for isotropic liquid and the same concentrations of surfactant and alcohol with 1.5 wt.% NaCl for birefringent liquid).

compared. To obtain the effect of the microstructure of the liquid on thermal diffuaivity, the effect of NaCl concentration on thermal diffuaivity was estimated because the only difference in the two aqueoua aolutiona waa NaCl concentration. The thermal conductivity of an ionic solution can be accurately estimated within ±5% using the following equation (242-245):

$$K_m\ (20^oC) = K_{water}\ (20^oC) + \Sigma\ \sigma_i\ C_i/4.186 \qquad (5\text{-}11)$$

where K_m = thermal conductivity of ionic aolution at 20°C (cal/cm aec K)

K_{water} = thermal conductivity of water at 20°C (cal/cm sec K)

C_i = concentration of electrolyte (gmol/K)

σ_i = coefficient that is characteristic of each ion.

The values of σ_i are 0 for Na^+ and -5.466×10^{-5} for Cl^- (156). The estimated thermal conductivities at 20°C were 0.1429×10^{-2} cal/cm sec K (= 0.3457 Btu/ft hr°F) for the brine containing 0.5 wt.% NaCl and 0.1427×10^{-2} cal/cm sec K (=0.3451 Btu/ft hr°F) for the brine containing 1.5 wt.% NaCl uaing the known value of K_{water} (20 °C) = 0.1430×10^{-2} cal/cm sec K (= 0.3459 Btu/ft hr °F). To estimate thermal conductivity at 40°C at which the experimenta were done, the following equation was uaed which was known to be accurate within ±5% except for atrong acids and alkalia at high concentrationa (156):

$$K_m\ (T) = K_m(20^oC)\ K_{water}(T)\ /\ K_{water}(20^oC). \qquad (5\text{-}12)$$

Using the known value K_{water} (40 °C) = 0.3648 Btu / hr ft °F, thermal conductivities at 40 °C were determined to be 0.3646 Btu / ft hr °F for the brine containing 0.5 wt.% NaCl and 0.3640 Btu / ft hr °F for the brine containing 1.5 wt.% NaCl indicating that thermal conductivity of brine was not affected by the small difference in salt concentration. This is consistent with the experimental results for calcium chloride brine (246). Since thermal diffusivity is defined as $\alpha = K / \rho C_p$, thermal diffusivity was also calculated using the known density and heat capacity of brine at 40 °C. Densities were determined to be 0.9957 g/cm^3 (= 62.1613 lb/ft^3) for the 0.5 wt.% brine and 1.0025 g/cm^3 (= 62.5858 lb/ft^3) for the 1.5 wt.% brine at 40 °C (247). Heat capacities were 0.9947 Btu/lb °F for 0.5 wt.% brine and 0.9853 Btu/lb °F for 1.5 wt.% brine at 40 °C by interpolation using the known values (247). The estimated thermal diffusivities of the brines were 5.897 x 10^{-3} and 5.9028 x 10^{-3} ft^2/hr for 0.5 and 1.5 wt.% brine, respectively, at 40 °C compared to the literature value 5.901 x 10^{-3} ft^2/hr for water. Since the salt concentration in this study did not change the thermal conductivity or thermal diffusivity, the different microstructurea of the two aqueous solutions had to be reaponaible for the big difference in the thermal diffuaivitiea of the isotropic and birefringent liquida.

Figure 5-7 shows the experimental reaults for the two aqueous aolutiona again over a different range of time from Figure 5-6. It is interesting to note that there waa an inflection for the birefringent system at about 5500 seconds. This type of inflection

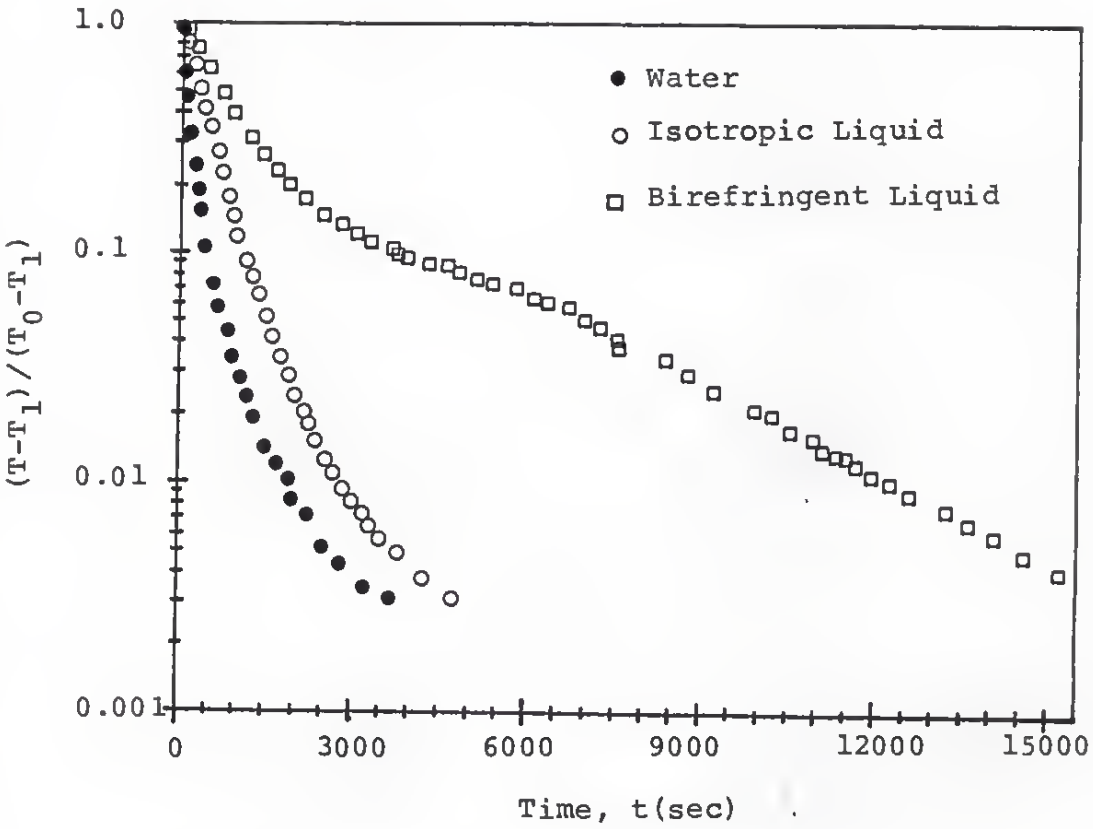


Figure 5-7. The change of temperature at the center for water, isotropic and birefringent liquids. TRS 10-80 (5 wt.%), isobutanol (3 wt.%) and brine (0.5 wt.% NaCl for isotropic liquid and 1.5 wt.% NaCl for birefringent liquid).

had not been observed for other liquids used in this study. Even though a clear explanation is not available at present, it might indicate a change in the property of the birefringent system at the correaponding temperature.

5.5 Thermal Conductivity of Microemulsions

In the earlier section, it was found that the microstructure of a liquid affected the thermal properties of the liquid. Since the microemulsion haa a unique microatructure compared to the molecularly mixed liquida, it is interesting to study the thermal properties of microemulsions. Therefore, thermal conductivity of microemulsions were measured and were compared to the values from the known equations for thermal conductivity of liquid mixtures. As a result, an empirical equation among the examined equations was suggested for the microemulaions.

The aamples uaed were w/o microemulaiona containing AOT, Arlacel20, mineral oil and different amounts of water. The thermal conductivity of the microemulsion was obtained from the measured thermal diffusivity, heat capacity, and density.

Table 5-4 and Figure 5-8 show the experimental values of thermal diffusivitiea while Figure 5-9 illuatratea the temperature changes as a function of time from which the thermal diffusivitiea were obtained. The thermal diffuaivity of microemulsion increased linearly aa the volume of water in the microemulaion increased, which was expected because thermal diffusivity of water (5.901×10^{-3} ft^2/hr) was much greater than that of mineral oil (2.841×10^{-3}

Table 5-4. Thermal Diffusivity of Mineral Oil, Mineral Oil Containing Surfactants and Alcohol-Free W/O Microemulsions at 40 °C

Liquid	W/O Ratio[a] (v/v)	Experimental Value (ft^2 / hr)	Average (ft^2 / hr)	Deviation (%)
Mineral Oil	0	2.915×10^{-3} 2.766×10^{-3}	2.841×10^{-3}	2.6
Mineral Oil[b] Containing Surfactants	0	2.882×10^{-3} 3.469×10^{-3}	3.176×10^{-3}	9.3
W/O-Microemulsion[c]	0.14	3.233×10^{-3} 3.591×10^{-3}	3.412×10^{-3}	5.3
	0.21	3.728×10^{-3} 3.967×10^{-3}	3.847×10^{-3}	3.1
	0.40	4.248×10^{-3} 3.986×10^{-3}	4.117×10^{-3}	3.2
	0.60	4.417×10^{-3}	4.417×10^{-3}	
	0.80	4.619×10^{-3} 4.936×10^{-3}	4.778×10^{-3}	3.3

a. The volume ratio of water to oil in a liquid sample.

b. 13%(w/v) Aerosol-OT and 27%(w/v) Arlacel 20 in mineral oil.

c. Microemulsion composition before the addition of water: 13%(w/v) Aersol-OT and 27%(w/v) Arlacel 20 in mineral oil.

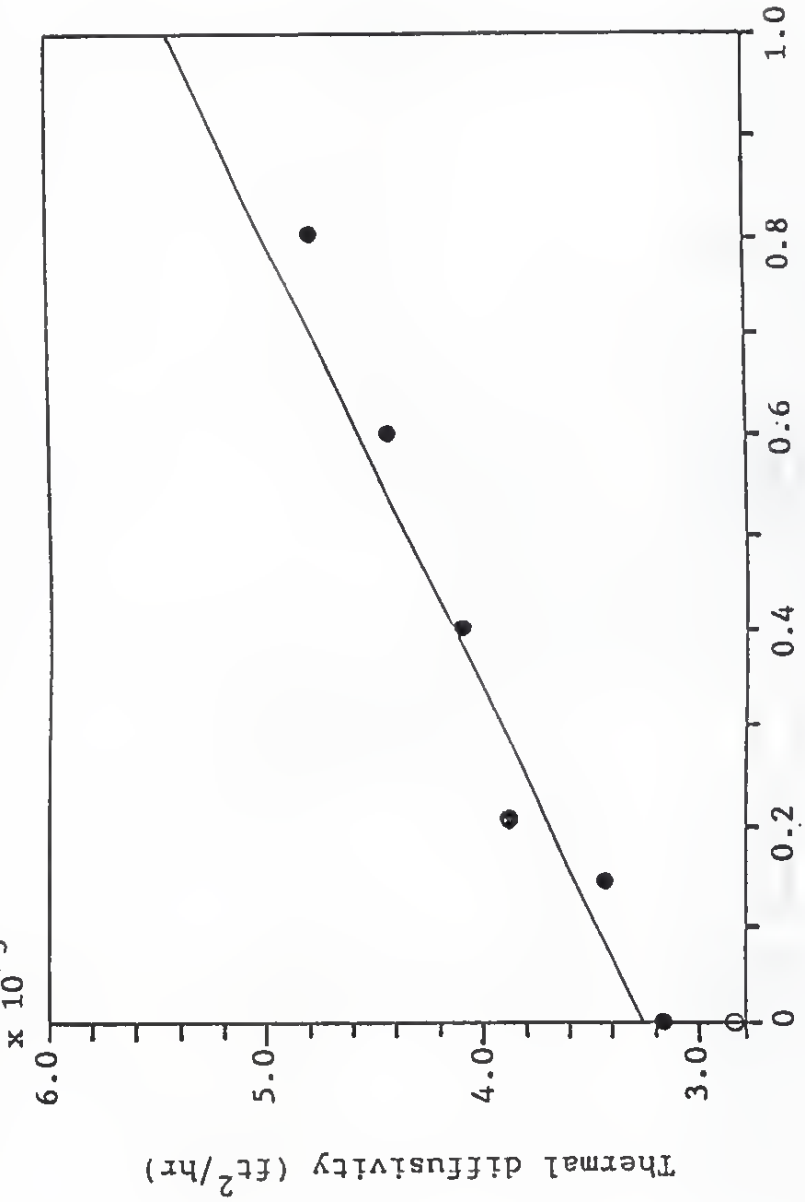


Figure 5-8. Thermal diffusivity of microemulsion depending on the water content. Microemulsion contained 0.13 g of Aerosol-OT and 0.27 g of Arlacel 20 in 1 ml of mineral oil with water.

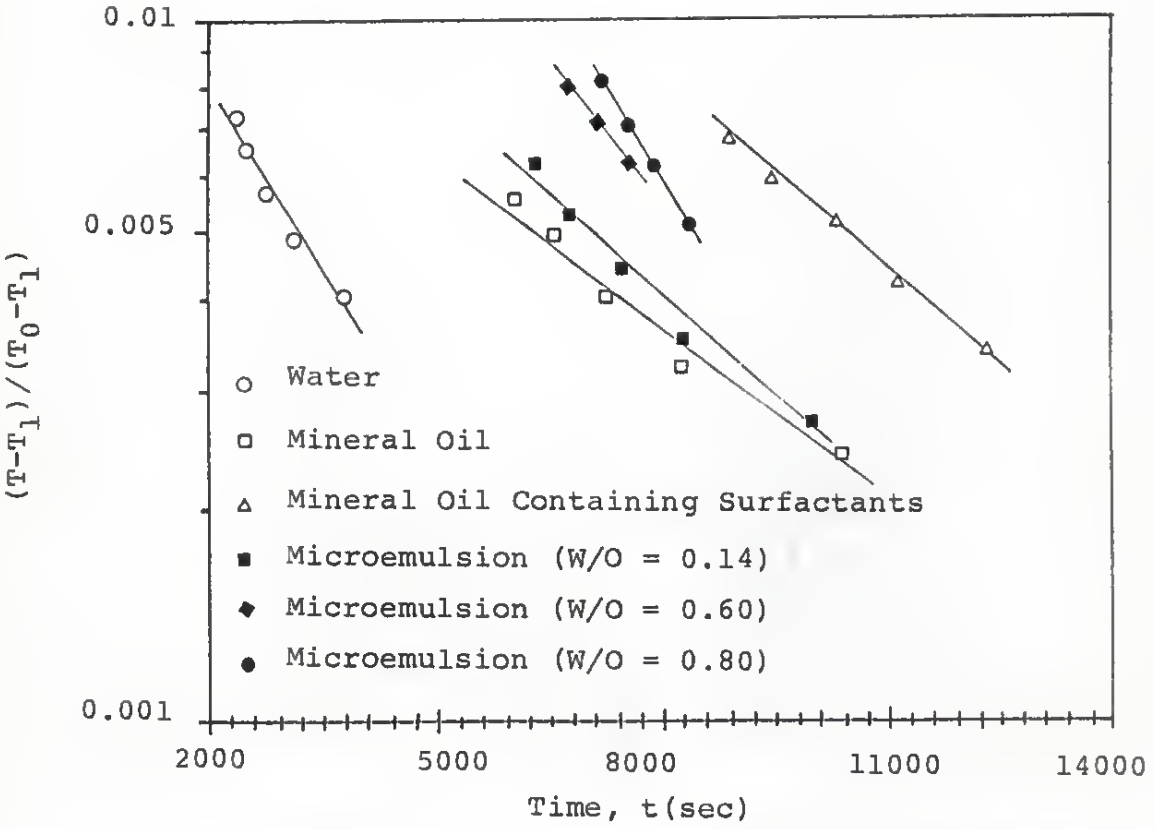


Figure 5-9. The change of temperature at the center for liquid samples. Microemulsions contained 0.13 g of Aerosol-OT and 0.27 g of Arlacel 20 in 1 ml of mineral oil with water.

ft^2/hr). The experimentally obtained value for mineral oil is reasonable compared to the literature values of the mineral oils used as heating media (232, 234). Table 5-5 and Figure 5-10 show the heat capacity of the microemulsion at different temperatures and different amounta of water. Heat capacity increaaed as temperature or an amount of water increased. As mentioned earlier, heat capacity at $40^{\circ}C$ waa obtained by a linear interpolation using the data ahown in Figure 5-10. Since the only practical recourae at present for calculating the heat capacity of mixture of solids, liquids, or gases ia to estimate it from that of the pure components on the basis of weight, mole, or volume fraction (247), the experimental values were compared to the estimated values using the following two equations:

$$C_{p,m} = C_{p,w} W_w + C_{p,o} W_o + C_{p,s} W_s \qquad (5\text{-}13)$$

and $$C_{p,m} = C_{p,w} X_w + C_{p,o} X_o + C_{p,s} X_s \qquad (5\text{-}14)$$

where $C_{p,m}$ = heat capacity of the mixture

$C_{p,w}$ = heat capacity of water

$C_{p,a}$ = heat capacity of surfactant

$C_{p,o}$ = heat capacity of oil

W_w, W_o, W_a = weight fractions of water, oil, and surfactant, reapectively

X_w, X_o, X_a = volume fractions of water, oil, and surfactant, respectively.

To use the above equationa, $C_{p,o}$ and $C_{p,a}$ at $40^{\circ}C$ were

Table 5-5. Heat Capacity of Mineral Oil, Mineral Oil Containing Surfactants and W/O Microemulsions at Different Temperatures

Liquid	W/O[a] Ratio	Heat Capacity (cal/gK)				
		37 °C	42 °C	47 °C	52 °C	57 °C
Mineral Oil	0.000	0.45386	0.45598	0.46045	0.45984	0.47810
Mineral Oil[b] Containing Surfactants	0.000	0.46426	0.46775	0.47318	0.48477	0.49524
Micro-emulsions[c]	0.136	0.50220	0.50743	0.51105	0.52244	0.53215
	0.212	0.52823	0.53234	0.53874	0.54888	0.55917
	0.400	0.57454	0.57864	0.58664	0.59894	0.61082
	0.600	0.61896	0.62149	0.62413	0.63559	0.64572
	0.800	0.65237	0.65550	0.66182	0.67486	0.69081

a. The volume ratio of water to oil in a liquid sample.

b. 13%(w/v) Aerosol-OT and 27%(w/v) Arlacel 20 in mineral oil.

c. Indicated amount of water added to the initial system: 13%(w/v) Aerosol-OT and 27%(w/v) Arlacel20 in mineral oil.

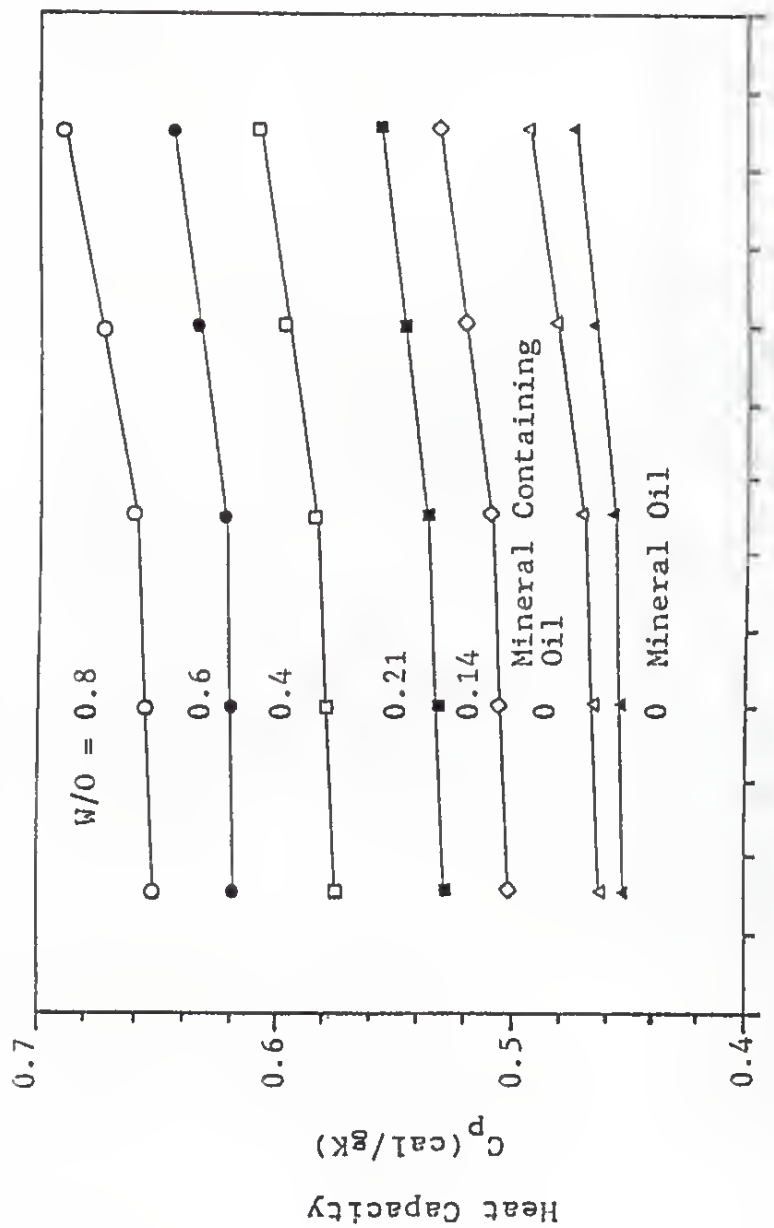


Figure 5-10. Heat capacity of microemulsion at different temperatures. Microemulsion contained 0.13 g of Aerosol-OT and 0.27 g of Arlacel 20 in 1 ml of mineral oil with water.

experimentally determined while the known value of $C_{p,w}$ was used: $C_{p,o}$ = 0.4551 Btu/lb^{o}F, $C_{p,s}$ = 0.4908 Btu/lb^{o}F and $C_{p,w}$ = 0.999 Btu/lb^{o}F. The equation based on the mole fraction could not be used because of the unknown molecular weight of mineral oil. Further, it is intuitively found that the mole fraction is not reasonable for w/o microemulsion because of both the high heat capacity and small molecular weight of water and low heat capacity and large molecular weight of mineral oil. As shown in Figure 5-11, equation 5-13 using the weight fraction could predict the heat capacities of the microemulsions within 3% while equation 5-14 using the volume fraction was valid within 2%. Both equations generated slightly higher values than the experimental values, consistent with previous findings. Finally, the thermal conductivities of the microemulsions obtained from the experiments were compared to the known equations.

The ideal method to predict the thermal conductivity of the liquid mixture is a mass fraction average of the pure component values (171):

$$K_m = \Sigma W_i K_i \qquad (5\text{-}15)$$

where W_i is mass fraction of component i and K_i is pure component thermal conductivity of component i.

The power law equation (156), a modification of the ideal equation, is:

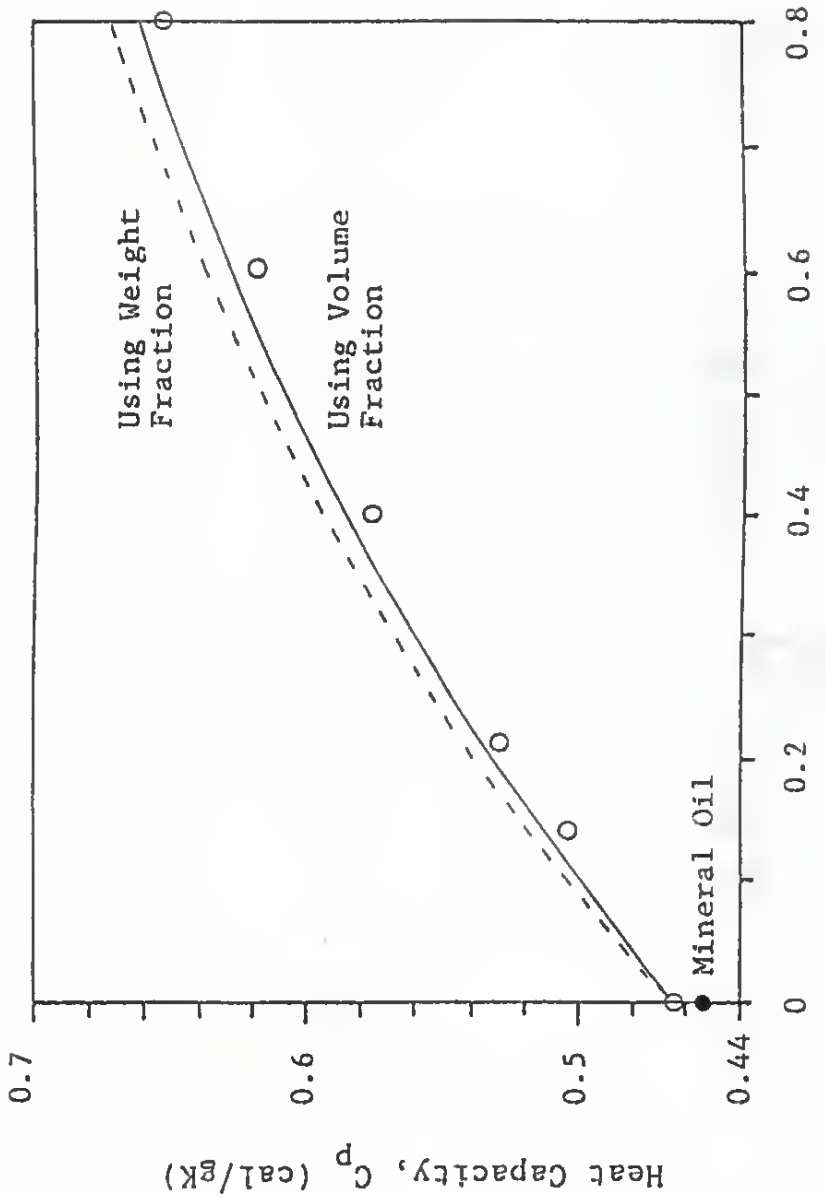


Figure 5-11. Heat capacity of microemulsion at 40 ^{o}C. Dotted and solid lines are predicted values from ideal equation using weight fraction (equation 5-13) and volume fraction (equation 5-14), respectively. Microemulsion contained 0.13 g of Aerosol-OT and 0.27 g of Arlacel 20 in 1 ml of mineral oil with water.

$$(K_m)^r = \Sigma W_i (K_i)^r \qquad (5\text{-}16)$$

where r is the parameter which fits the data best. It has been known that a value of r = -2 is reasonable for most systems(156). Further, Rowley and White (171) examined the known equations to estimate thermal conductivity of ternary liquid mixtures using the experimental data of thermal conductivity of molecularly mixed liquids such as benzene - normal pentane - cyclohexane, benzene - chloroform - (2-propanol), toluene - benzene - normal pentane, cyclohexane - carbon terachloride - (2-propanol) and normal pentane - toluene - (2-propanol) mixtures. They found that the power law equation with r = -2 gave the most consistent results for these mixtures while the ideal model yielded unsatisfactory predictions. When r = -2, equation 5-16 becomes :

$$(K_m)^{-2} = \Sigma W_i (K_i)^{-2}. \qquad (5\text{-}17)$$

The Li equation (168) and the local composition model (172) were not considered here because some of their required parameters could not be determined.

Three equations were known for the macroemulsions. Wang and Knudsen (248) derived the equations considering the emulsion to be made of uniform filaments of oil and water arranged parallel to or perpendicular to the direction of heat flow:

$$K_m = X_w K_w + X_o K_o \qquad (5\text{-}18)$$

and $$(K_m)^{-1} = X_w (K_w)^{-1} + X_o (K_o)^{-1} \qquad (5\text{-}19)$$

where K_w and K_o = thermal conductivities of water and oil, respectively, and X_w and X_o = volume fraction of water and oil, respectively.

Tareef (249) also derived the equation for the macroemulsions considering that the thermal field in a two-phase system was analogous to the electrical field in a similar system:

$$K_m = K_c \frac{[2K_c+K_d-2\ \phi_d(K_c-K_d)]}{[(2K_c+K_d+\ \phi_d(K_c-K_d)]} \qquad (5\text{-}20)$$

where K_c and K_d = thermal conductivities of the continuous and the discontinuous phase, respectively, and ϕ_d = volume fraction of the discontinuous phase.

Table 5-6 and Figure 5-12 show the experimental and the predicted values of the thermal conductivities of the microemulsions. As mentioned earlier, the thermal conductivities were obtained from the experimental data of thermal diffusivities, heat capacities, and densities at 40°C using the definition of thermal diffusivity, $\alpha = K / \rho C_p$. The average value of the thermal diffusivities were used for calculation. The surfactants were considered in the discontinuous phase (water) for equations 5-18, 5-19 and 5- 20. The thermal conductivity of the surfactants was estimated from the data for mineral oil containing surfactants using equation 5-15, and K_s was 1.196×10^{-3} Btu/hr ft°F.

Table 5-6. Experimental and Predicted Values for Thermal Conductivity of Mineral Oil, Mineral Oil Containing Surfactanta and W/O Microemulsions by Known Equations (at 40 ^{o}C)

(a) Experimental Values

Liquid	W/O[a] Ratio	α (x10^3 ft^2/hr)	ρ (lb/ft^3)	C_p (Btu/lb F)	K_m^e (x10^3 Btu/ft hr)
Mineral Oil	0.00	2.841	54.246	0.45513	7.014
Mineral Oil Containing Surfactanta[b]	0.00	3.176	57.874	0.46635	8.572
Micro-emulsions[c]	0.14	3.412	58.481	0.50534	10.083
	0.21	3.847	58.799	0.5370	12.005
	0.40	4.117	59.070	0.57700	14.032
	0.60	4.417	59.622	0.62048	16.340
	0.80	4.778	59.929	0.65429	18.734

(continued)

Table 5-6 -continued

(b) Comparison of Predicted Values of W/O Microemulsions by Known Equations with Experimental Values

W/O[a] Ratio	K_m = ($\times 10^3$ Btu/ft hr), Error = (%)									
	Ideal		Power		Wang-a[d]		Wang-b[e]		Tareef	
	K_m	Error	K_m	Error	K_m	Error	K_m	Error	K_m	Error
0.14	11.479	+13.9	8.276	-17.9	10.900	+8.1	8.856	- 8.7	9.851	-9.5
0.21	12.738	+6.1	8.468	-29.5	12.051	+0.4	9.243	-23.0	10.561	-12.0
0.40	15.614	+11.3	8.965	-36.1	14.759	+5.2	10.173	-27.5	12.233	-12.8
0.60	17.993	+10.1	9.454	-42.1	17.070	+4.5	11.049	-32.4	13.730	-15.9
0.80	19.929	+6.4	9.913	-47.1	18.969	+1.3	11.855	-36.7	15.038	-19.7

a.The volume ratio of water to oil in a liquid sample.

b. 13%(w/v) Aerosol-OT and 27%(w/v) Arlacel 20 in mineral oil.

c. Indicated amount of water added to the initial system: 13%(w/v) Aerosol-OT and 27 %(w/v) Arlacel 20 in mineral oil.

d. $K_m = X_w K_w + X_o K_o$

e. $K_m^{-1} = X_w K_w^{-1} + X_o K_o^{-1}$

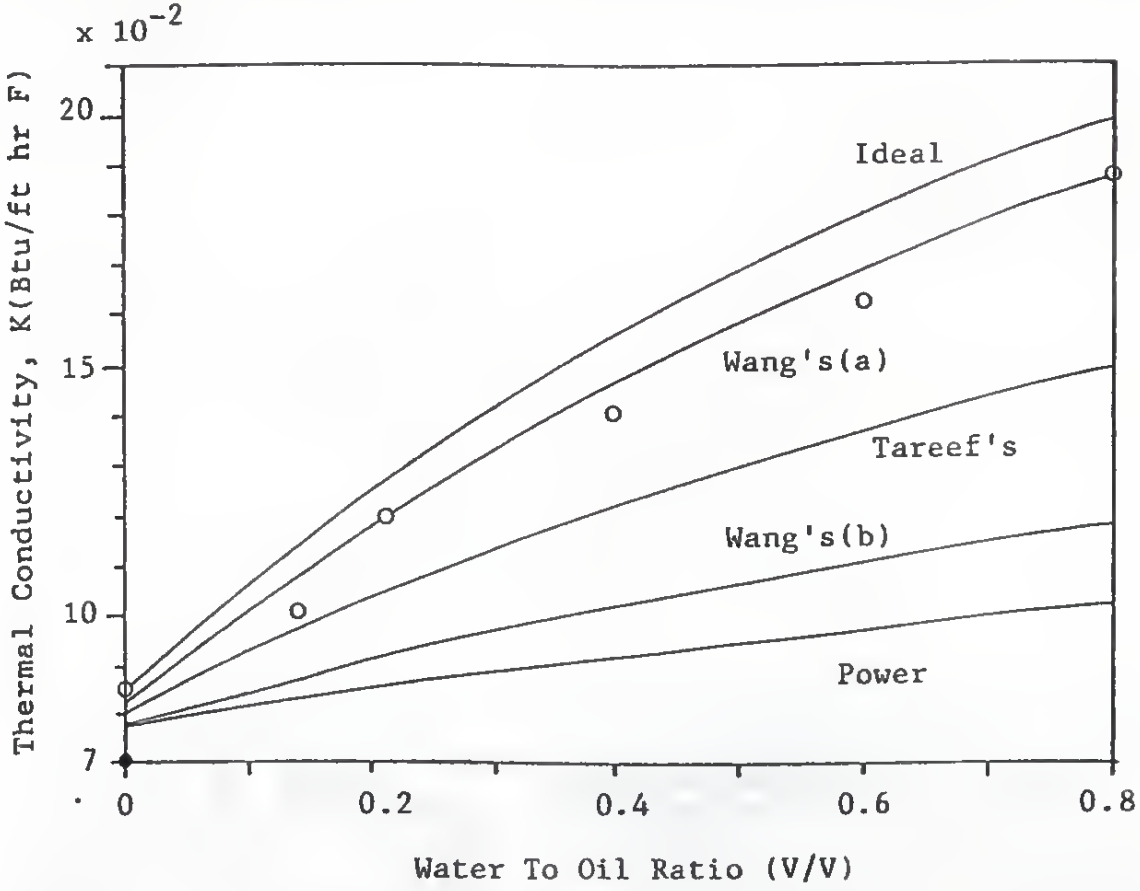


Figure 5-12. Thermal conductivity of microemulsion at 40 °C. Solid lines are predicted values from the known equations. Wang's (a) and (b) are equations 5-18 and 5-19, respectively. Microemulsion contained 0.13 g of Aerosol-OT and 0.27 g of Arlacel 20 in 1 ml of mineral oil with water.

The power law equation 5-17 gave the poorest resulta among the equations uaed, indicating that a value other than -2 should have used for r. Since r = -2 was known to be reasonable for the usual liquid mixtures (156, 171), it may be that the microstructure of the microemulsion is very different from molecularly mixed liquida and the thermal conductivity of the microemulsion cannot be predicted using the existing equations for molecularly mixed liquids. The ideal model was, surprisingly, much better than the power law model when r = -2, but still gave higher values than the experimental values. The equations for the macroemulsion (except the equation 5-18) gave lower values than the experimental values. The large error of equation 5-18 for a microemulaion whose w/o = 0.14 as shown in Table 5-6 (b), seemed to be caused by the assumption that the surfactants were in discontinuous phase (water) because a lot of surfactants at w/o = 0.14 were possibly in the continuous phase (oil). The accuracy of the prediction using the equations for the macroemulsion decreased in the order of equations 18, 20 and 19.

5.6 Conclusiona

This chapter can be aummarized as follows:

1. The aimple unsteady-state method to meaaure the thermal diffusivity of liquids waa developed and uaed in this study: the method is aimple and inexpenaive but requires a large amount of aample and a long experimental time.

2. The thermal conductivity of the liquid waa obtained from the meaaurements of thermal diffuaivity, denaity, and heat capacity of the sample.
3. The effect of the microstructure of the liquid on the thermal propertiea was investigated using two liquid samples which differed in their microstructure: the thermal diffusivity of the isotropic system was 20% greater than that of the birefringent system, indicating that the microstructure of the liquid affected its thermal properties.
4. Thermal conductivity of the microemulsion could not be well predicted by ideal equation compared to one of the equations for macroemulsions by Wang and Knudsen which predicted very accurately the thermal conductivities of the microemulsion.
5. The worst prediction waa by the power law with r = -2 which is the common value of r for the uaual molecularly mixed liquids. The results suggest that the microstructure of the microemulsion ia much different from that of molecularly mixed liquids.

CHAPTER 6

STABILITY OF METHANOL-ISOOCTANE-TOLUENE MIXTURES AT -25°C

6.1 Introduction

Gasoline has aerved as a fuel for automobiles for many decades. However, the energy criais of recent years has generated the neceasity for alternate and mixed fuels. A possible mixed fuel ia a mixture of an alcohol and hydrocarbona. Eapecially addition of methanol, itself a fuel, to gasoline strechea the gasoline supply (191). The state of California already approved the use of the mixture of methanol and gasoline as an automobile fuel and Arco company ia ready to sell the mixed fuel (177). Two other states, Arizona and Colorado, are also considering the use of the mixed fuel as an automobile fuel. Further, several automakers are developing methanol-compatible vehicles because of its better efficiency in addition to the economic advantages it offera (177, 250). However, the problem of the phase separation at and below 0°C must be resolved in order to use thia mixture as a fuel for automobiles even under the cold weather conditions (190).

The condition for instability of a liquid mixture dependa on the nonideality of the solution at a given temperature (251). However, two immiacible or partially miacible liquida can be converted into a single phase liquid in the apecific range of

compositions and temperatures when an appropriate third component is added to the mixture. Especially, the surface active agents such as the surfactants and the alcohols are known to form the microemulsions with two immiscible liquids, for example, hydrocarbons and solvents such as water, methanol, grycol, formamide, glycol, etc. (8, 10, 17, 252, 253).

In this study, the effect of additives (surfactants and/or alcohols) on the stability of the methanol-isooctane-toluene mixture was investigated at the low temperatures ($-25^{\circ}C$).

6.2 Materials and Methods

The chemicals used in this study are shown in Table 6-1. All chemicals were used as received.

A great many methods have been described for the preparation and maintenance of low-temperature bath (254). Among the simpler techniques, dry ice and carbon tetra chloride appeared to be the best for this study. Solid lumps of dry ice in a Dewar flask containing carbon tetrachloride maintained the bath at reasonably uniform temperature and low viscosity. The bath was not, of course, a system at equilibrium: a layer of solid carbon tetrachloride appeared to form over the dry ice and a steady state was obtained with slow evolution of gaseous CO_2. A small amount of dry ice crushed into fine particles was continuously added and agitated until it formed a slush giving the desired temperature, $-25^{\circ}C$. The bath had been generally maintained at $-25\pm1^{\circ}C$ if they had been

Table 6-1. Chemicala Uaed for the Study of Phase Stability of 50%(v/v) Methanol-40%(v/v) Isooctane-10%(v/v) Toluene Mixture at -25 °C

Chemicala	Company	Grade	Water[a]	Structure[b]
Methanol	Fisher	Certified	0.158	
Methanol	Fisher	Purified	0.250	
Isooctane	Philips	Spectro	0.028	
Toluene	Fiaher	Certified	0.180	
Carbon tetra-chloride	Fiaher	Certified		
Karl Fisher[c] reagent	Fiaher			
Ethanol	Fiaher	Denatured	4.863	
N-propanol	Fiaher	Certified	1.157	
2-propanol	Fisher	Certified	0.492	$CH_3CHOHCH_3$
N-butanol	Fiaher	Certified	0.692	
Isobutyl alcohol	Fiaher	Certified	0.667	$(CH_3)_2CHCH_2OH$
2-butanol	Mallinckrodt	Organic	1.242	$CH_3CH_2CHOHCH_3$
N-pentanol	Fiaher	Certified	1.208	
3-pentanol	Kodak	Reagent	1.400	$CH_3CH_2CHOHCH_2CH_3$
Isoamyl alcohol	J.T.Baker	Analyzed	0.020	$(CH_3)_2CH(CH_2)_2OH$
Tert-amyl alcohol	Fiaher	Reagent	1.388	$(CH_3)_2C(OH)CH_2CH_3$
N-hexanol	Kodak		0.775	
2-hexanol	Kodak		2.967	$CH_3CHOH(CH_2)_3CH_3$
N-heptanol	Fisher	Certified	1.379	
4-heptanol	Kodak		2.000	$CH_3(CH_2)CHOH(CH_2)_2CH_3$

Table 6-1 -continued

Chemicals	Company	Grade	Water[a]	Structure[b]
N-octanol	Fisher	Certified	1.088	
2-octanol	Kodak		1.975	$CH_3CHOH(CH_2)_5CH_3$
N-nonanol	Kodak		0.800	
N-decanol	Aldrich	99%	0.492	
N-doecanol	Kodak		0.625	
Arlacel 83	ICI			Sorbitan Sesquoleate
Arlacel 186	ICI			Mono- & diglycerides
Brij 30	ICI			Polyoxyethylene(4) lauryl ether
Brij 30sp	ICI			Polyoxyethylene(4) lauryl ether[d]
Tween 81	ICI			Polyoxyethylene(5) sorbitan monooleate
CO 520	GAF			$CH_3(CH_2)_8$- -$O(CH_2CH_2O)_4(CH_2)_2OH$
Lauric acid	Baker			$CH_3(CH_2)_{10}COOH$
Myristic acid	K&K			$CH_3(CH_2)_{12}COOH$
Palmitic acid	Baker			$CH_3(CH_2)_{14}COOH$
Oleic acid	Fisher			$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

a. Water in the chemical (mg / ml chemical)

b. Structurea of well-known chemicala are omitted.

c. Mixture of iodine, aulfur dioxide, pyridine and glycol.

d. Contains 0.01% BHA and 0.01% citric acid.

agitated intermittently and if only a amall excess of dry ice had been used. The temperature of the sample was measured by an alcohol thermometer. The alcohol thermometer was periodically checked uaing the thermocouple probe manufactured and calibrated by Atkins Technical Co. at the beginning of the experiments.

Two methoda were employed for each alcohol: the titration and the grid point methods (215, 255). For the titration method, 50% methanol, 40% iaooctane, and 10% toluene by volume at room temperature were mixed in a graduated tube and it was placed in a dryice-carbon tetrachloride bath. After the temperature of the sample reached at $-25^{\circ}C$, an alcohol was added drop by drop while the mixture waa agitated by a glass rod. After the each addition of a drop of a alcohol, the mixture was taken out from the bath and was visually examined whether it was turbid or not. If the mixture was clear after agitation, the mixture was placed in the bath for 10 additional minutes to check whether it remained as a single phase or formed two phases. The amount of an alcohol required to form one phase of the mixture was determined when the mixture was clear upon agitation and remained as a single phase at $-25^{\circ}C$. A turbid mixture after each addition of an alcohol always formed two phases upon standing still while a clear mixture after addition of an alcohol always remained aa a single phase. During the experiments, the temperature of the sample was continuously monitored and a small exceaa of dry ice was added to maintain the bath at $-25^{\circ}C$ whenever necessary. The results from the titration method were used to select compositions for grid point method. For the grid point

method, the several samples having different amounts of an alcohol were prepared in the graduated tubes based on the results of the titration method. Every sample was initially a total 10 ml at room temperature before an addition of an alcohol. The increment in an amount of an alcohol was 0.1 ml at room temperature for an alcohol being examined. The sample tubes were placed in the bath. After 30 minutes in the bath, each sample was checked whether it was one or two phases. If the two phases were formed, the volume ratio of upper to lower phase at $-25^{\circ}C$ was recorded. The results of the two methods were in reasonable agreement.

To determine the amount of water in the used chemical, Karl Fisher reagent method (256) was employed. This method determines free water and water of hydration in most solids or liquid organic and inorganic compounds. A sample (20-50 ml) was titrated with Karl Fisher reagent, which was a mixture of iodine, sulfur dioxide, pyridine, and methanol or glycol ether. As long as any water was present in the sample, the iodine was reduced to colorless hydrogen iodine. The end point was the first appearance of free iodine and determined visually: the end point was taken during the titration when the color changed from yellow to orange-red and persisted for at least 30 seconds. The measurements were repeated at least twice for each chemical used. The Karl Fisher reagent was standardized before measurements using water-in-methanol standards. The water content of the sample was calculated using the following equation:

$$\text{Water(mg/ml aample)} = A\ F\ /\ W \qquad (6\text{-}1)$$

where A = ml of reagent required for titration of the sample, F = water equivalent, in mg of water per ml of Karl Fisher reagent, and W = volume of the aample in ml at room temperature.

The equilibrium compositions for the aystem with normal pentanol as an additive were studied by a gas chromatography (GC). After equilibrium, the upper phase was taken and analyzed by Hewlett Packard GC 5840. The sample was diluted by aceton before the injection into the GC and the injection amount was 3 to 4 μl. Separation was obtained on a 49 m x 0.3 mm capillary column packed with 5% phenyl methyl silicon (SE-54). The column temperature waa increased at 6 °C/min and detection was carried out by flame ionization. The carrier gas waa helium. Since the senaitivity was different for each component, the relative sensitivity chart (257) was used. The weight percent of each component was, then, obtained using the following equation:

$$\%A = (\text{area } A\ /\ F_A)\ /\ (\Sigma\ \text{area}\ /\ F)\ \times\ 100 \qquad (6\text{-}2)$$

where %A = weight percent of the component A and F_A = relative senaitivity of the component A. The weight was converted to the volume from the density data (258).

6.3 Effect of the Chain Length of Alcohola

As shown in Figure 6-1, the mixture was aeparated as two phases with the volume ratio of the upper to the lower phase, 0.54, at

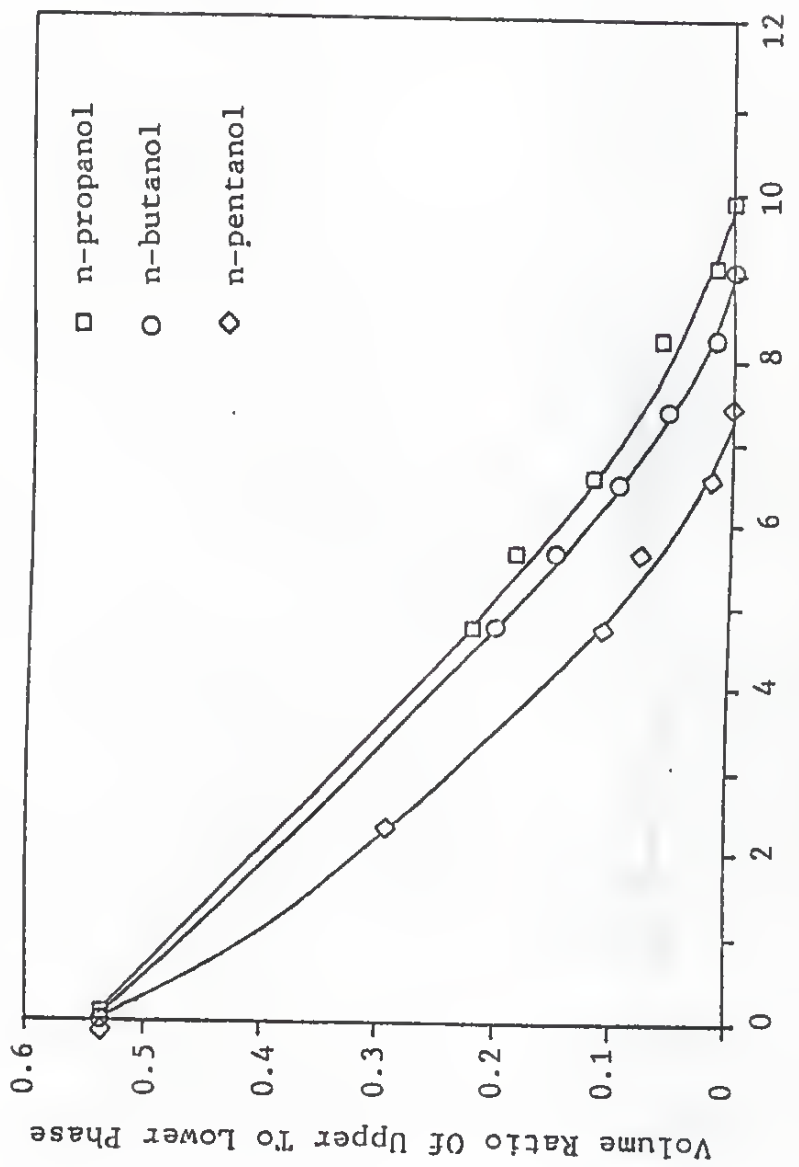


Figure 6-1. Effect of normal alcohol on the stability of the methanol-isooctane-toluene mixture at -25°C.

-25 °C. The lower phase started to grow as an amount of the added normal alcohol increased. Upon adding more alcohol, eventually the mixture became a single phase at -25 °C. Further, the required amount of the normal alcohol decreased as the number of carbon atoms of the normal alcohols increased from 3 to 5. The rate of growth of the lower phase also increased as the number of carbon atoms increased. Figure 6-2 show the relationship between the required amount of the normal alcohol to form a single phase at -25 °C and the number of carbon atoms of the normal alcohols ranging from 2 to 12. The required amount of the normal alcohol decreased up to normal octanol and then leveled off. Most significant decrease in the required amount of the normal alcohol occurred at the normal propanol: the required amount decreased from 50% for normal ethanol to 9.9% for normal propanol. It is interesting to note that the effect of the chain length of normal alcohol disappeared when the number of carbon atoms of the normal alcohol was equal to octane. The detailed data for the normal alcohols are shown in Figure 6-3 through Figure 6-9.

6.4 Effect of the Structure of Alcohols

Table 6-2 and Figures 6-10 and 6-11 show the relationship between the required amount of the secondary alcohols to form a single phase at -25 °C and the number of carbon atoms in the secondary alcohols. The trend in the relationship was similar to that of the normal alcohols: as the amount of the secondary alcohol

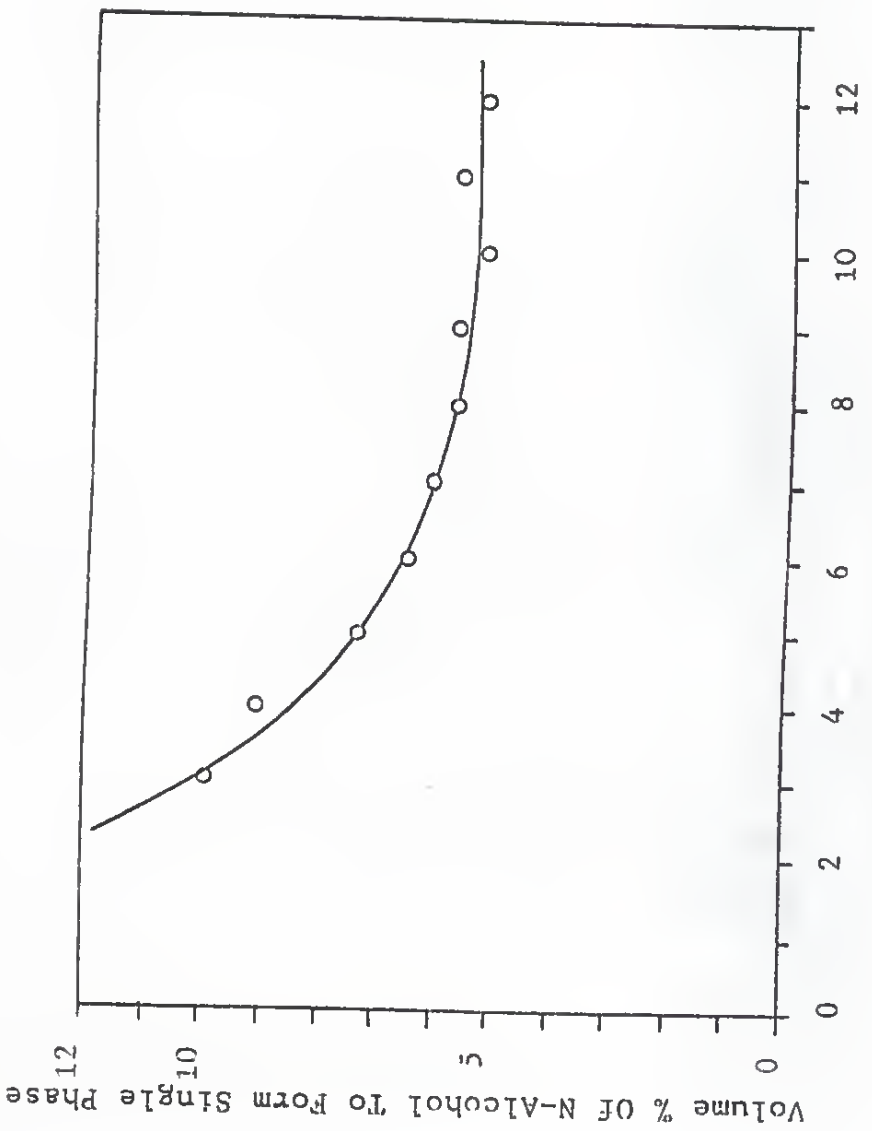


Figure 6-2. Required amount of normal alcohol to form single phase of the methanol-isooctane-toluene mixture at -25°C.

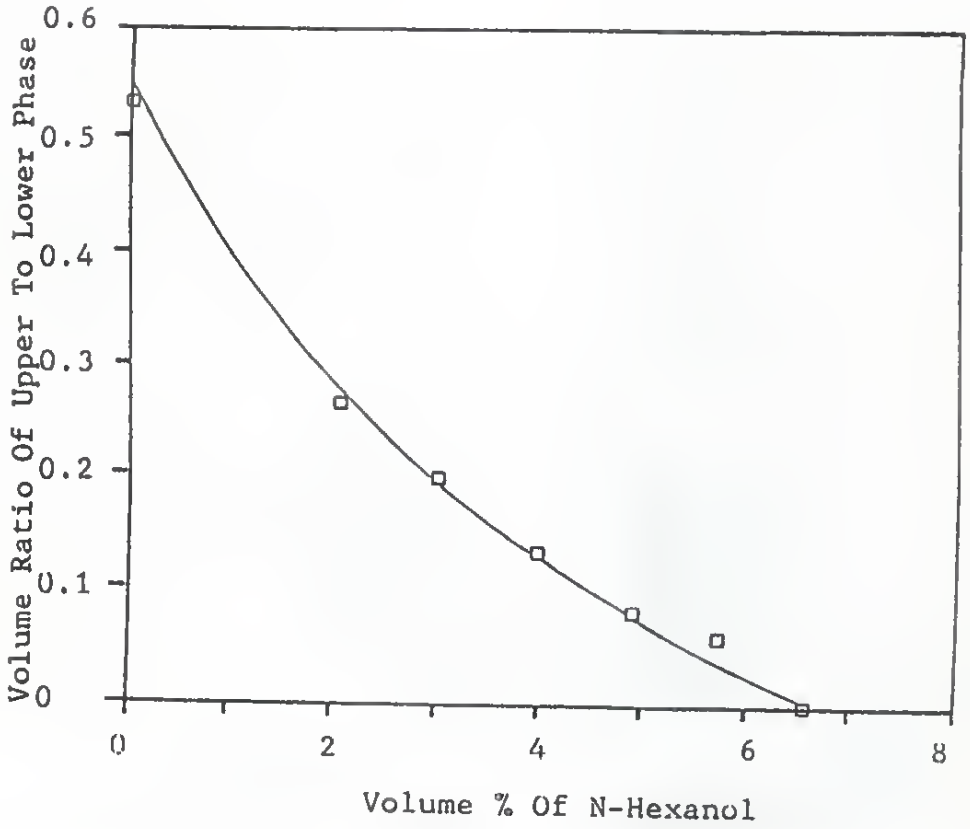


Figure 6-3. Effect of normal hexanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

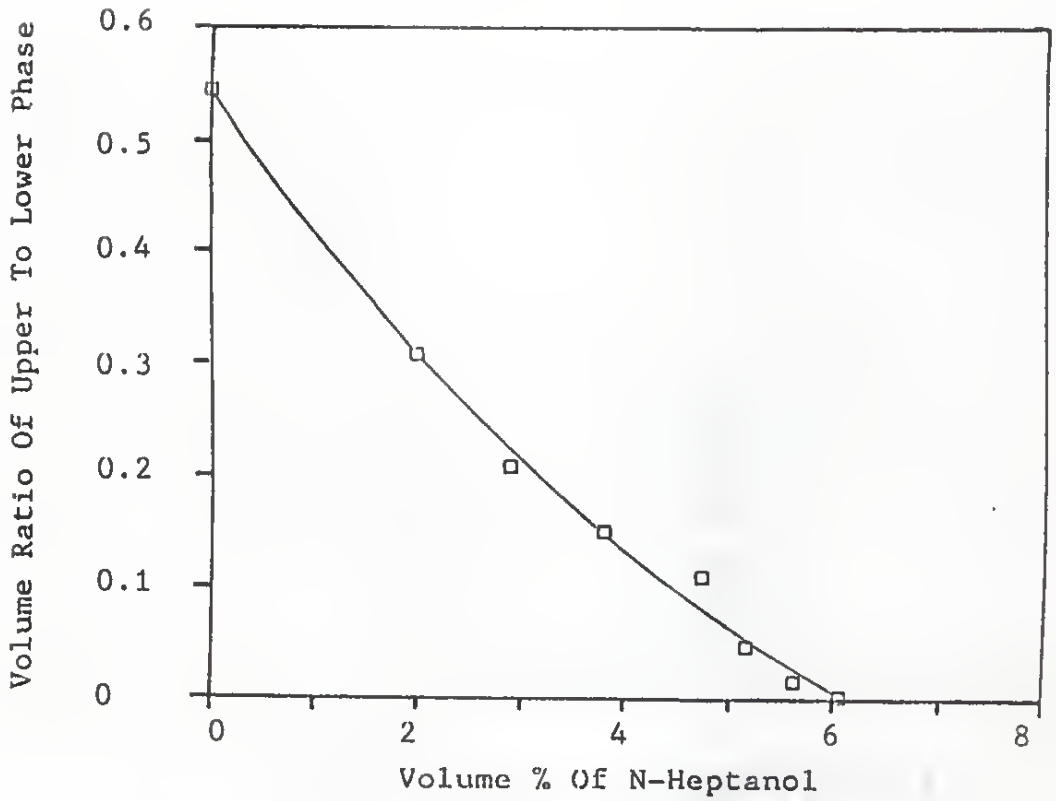


Figure 6-4. Effect of normal heptanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

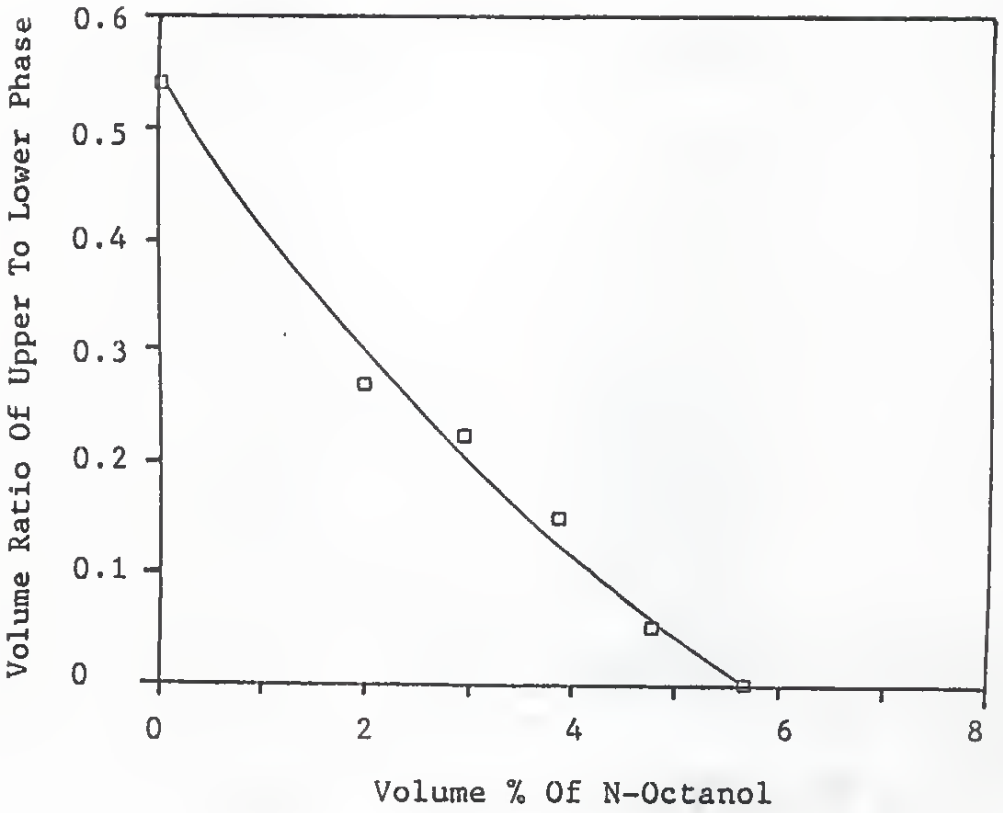


Figure 6-5. Effect of normal octanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

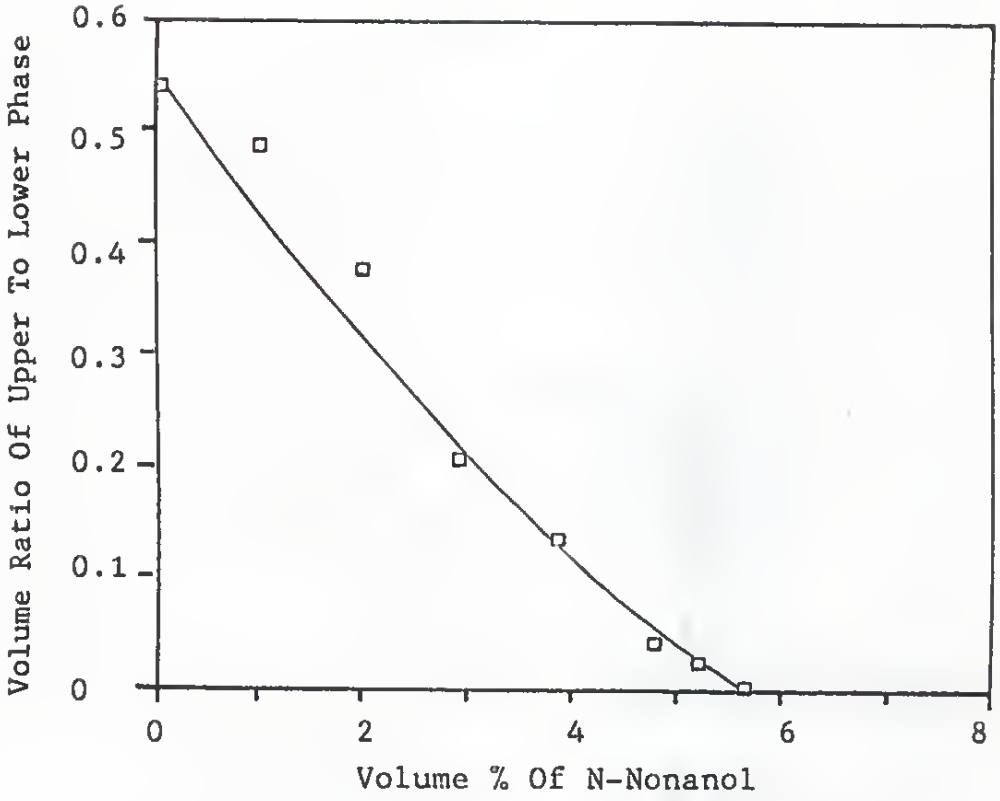


Figure 6-6. Effect of normal nonanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

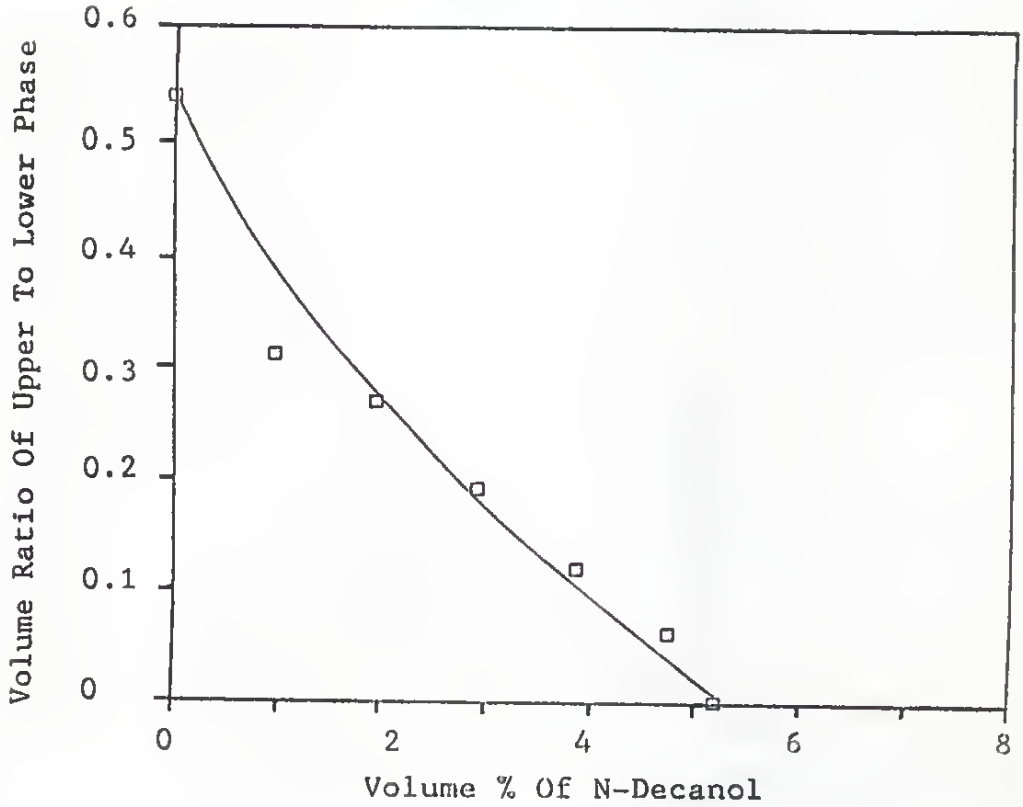


Figure 6-7. Effect of normal decanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

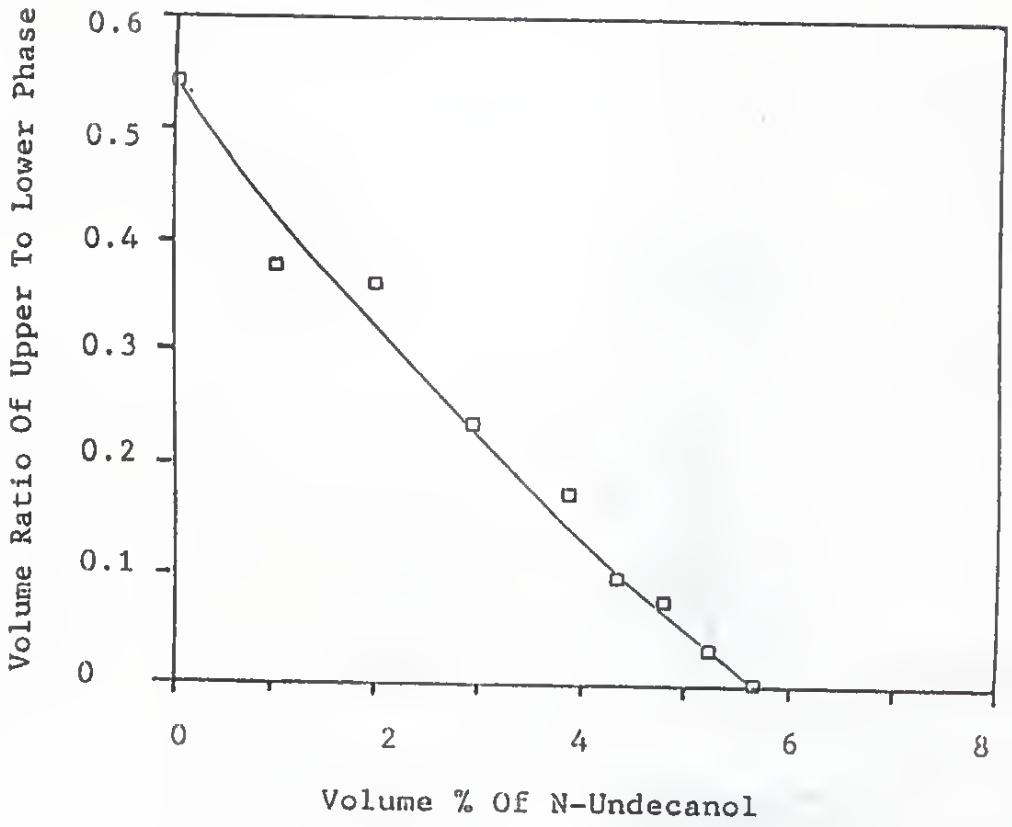


Figure 6-8. Effect of normal undecanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

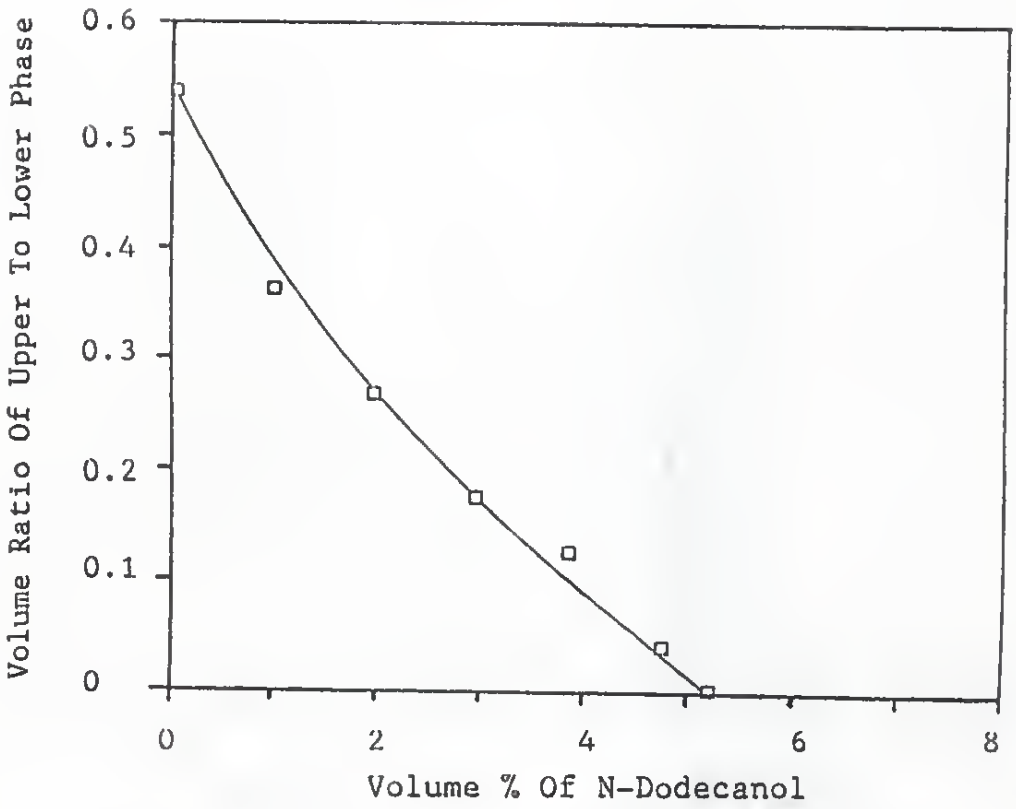


Figure 6-9. Effect of normal dodecanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

Table 6-2. Required Amounts of Alcohols to Form One Phase of 50%(v/v)Methanol-40%(v/v)Isooctane-10%(v/v)Toluene Mixture at -25 °C (Volume %)

Number of Carbon Atoms in Alcohol	2	3	4	5	6	7	8	9	10	11	12
N-alcohols	50.0	9.9	9.1	7.4	6.5	6.1	5.7	5.7	5.2	5.7	5.2
Secondary Alcohols											
2-alcohols		12.3	8.3	7.4	6.5	6.5					
3-alcohols				7.4							
Branched Alcohols											
Iso-alcohols			8.3	8.3							
Tert.-alcohols				8.3							

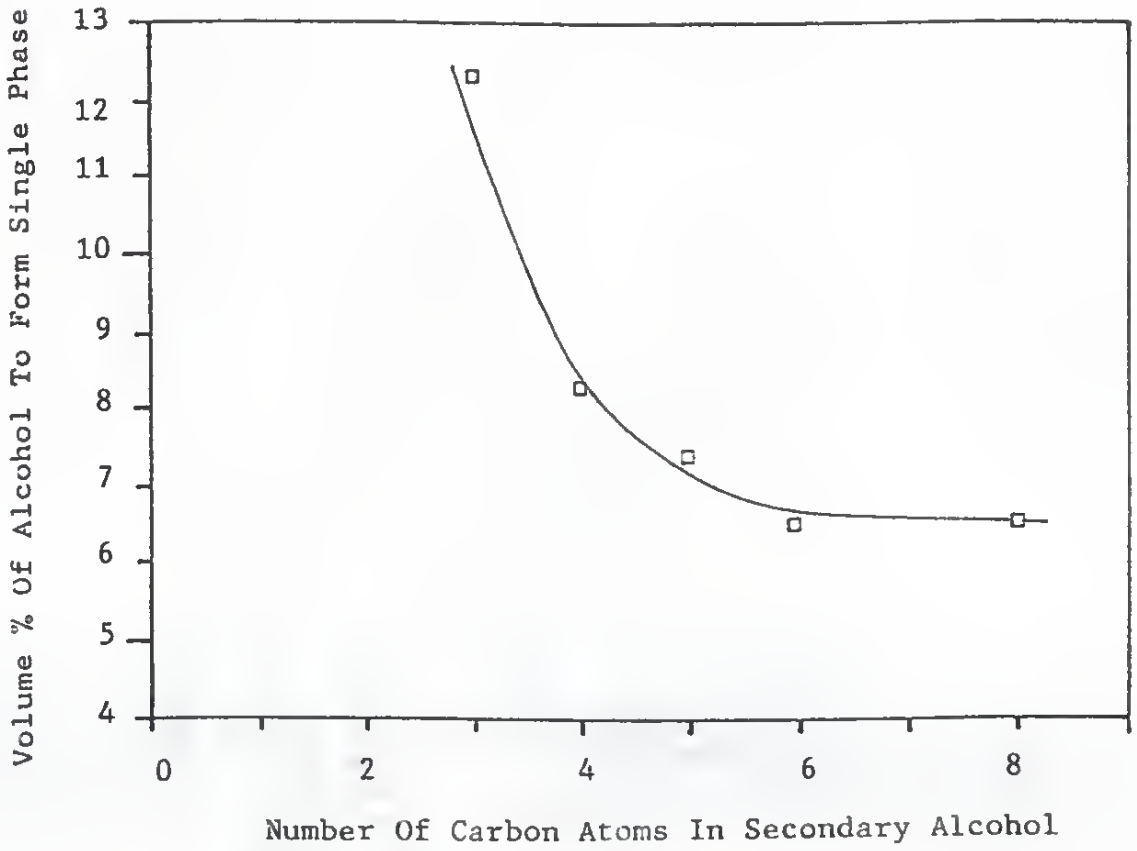


Figure 6-10. Required amount of the secondary alcohol to form the single phase of the methanol-isooctane-toluene mixture at $-25^{o}C$.

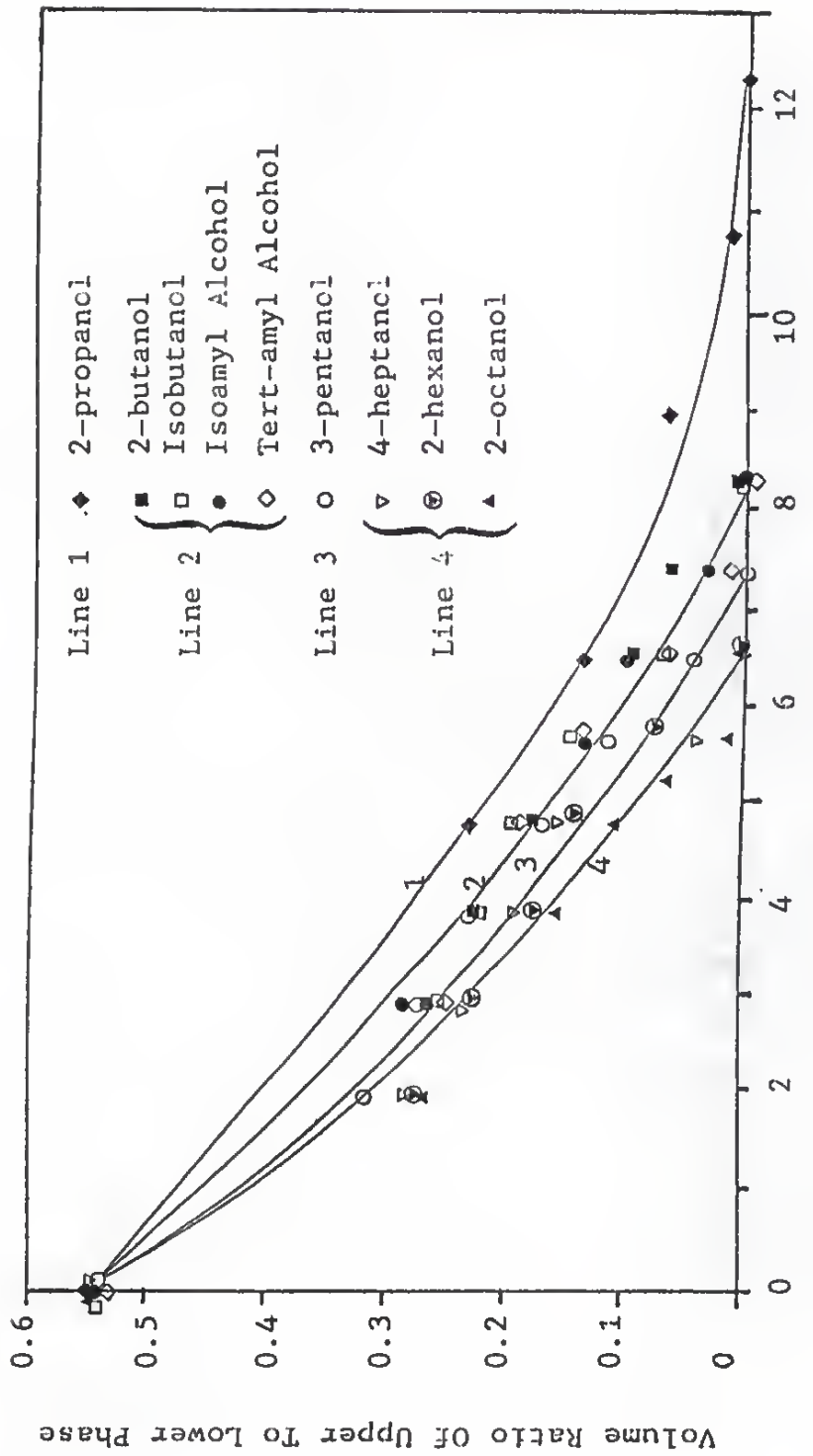


Figure 6-11. Effect of secondary and branched alcohol on the stability of the methanol-isooctane-toluene mixture at -25°C.

increased, the low phase grew and eventually the single phase was formed; the required amount of the secondary alcohol to form a single phase at -25 °C decreased as the number of carbon atoms increased. However, the effect of the number of carbon atoms in the secondary alcohol diminished faster than that in the normal alcohol compared 6 carbon atoms for the secondary alcohols to 8 carbon atoms for the normal alcohols. For the branched alcohols, the effect of the number of carbon atoms cannot be seen: as shown in Figure 6-11, all the branched alcohols can be presented by on line indicated by the line 2. For normal alcohols, secondary alcohols and branched alcohols, the amount of alcohol required for the formation of a stable phase, was invariant above C_8, C_6 and C_4, respectively. As seen in Table 6-2, no secondary and branched alcohol were more effective than the corresponding normal alcohols indicating that the straight chain is important. While the branched pentanols were less effective than the corresponding secondary pentanols, there was no difference between branched butanol and the secondary butanol. The detailed data for the secondary and the branched alcohols are shown in Figure 6-12 through Figure 6-20.

6.5 Effect of Surfactants

It is interesting to see the effect of the surfactant on the phase stability of the mixture at -25 °C, because the surface activity of the surfactant is greater than that of the alcohol (102). Among the used anionic surfactants in Table 6-1, only oleic acid made the hydrocarbon mixture as a single phase at -25°C without

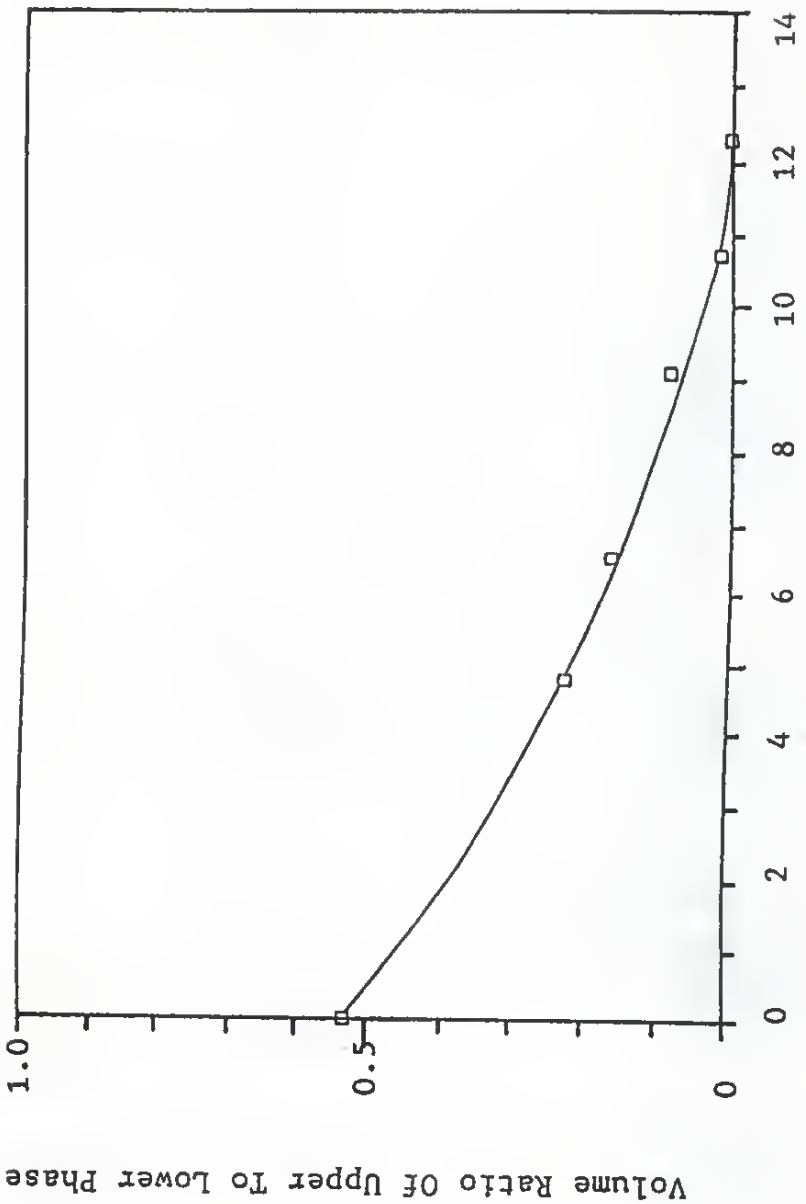


Figure 6-12. Effect of 2-propanol on the stability of the methanol-isooctane-toluene mixture at -25^{0}C.

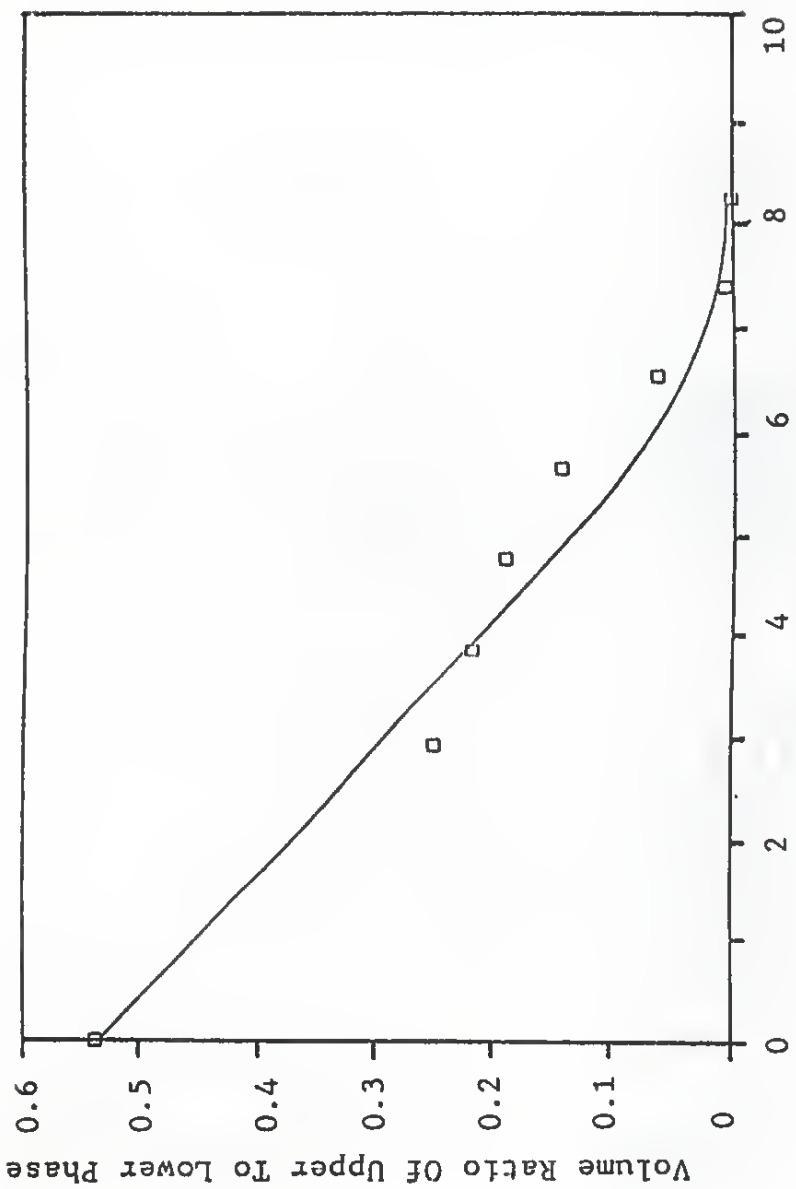


Figure 6-13. Effect of isobutanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

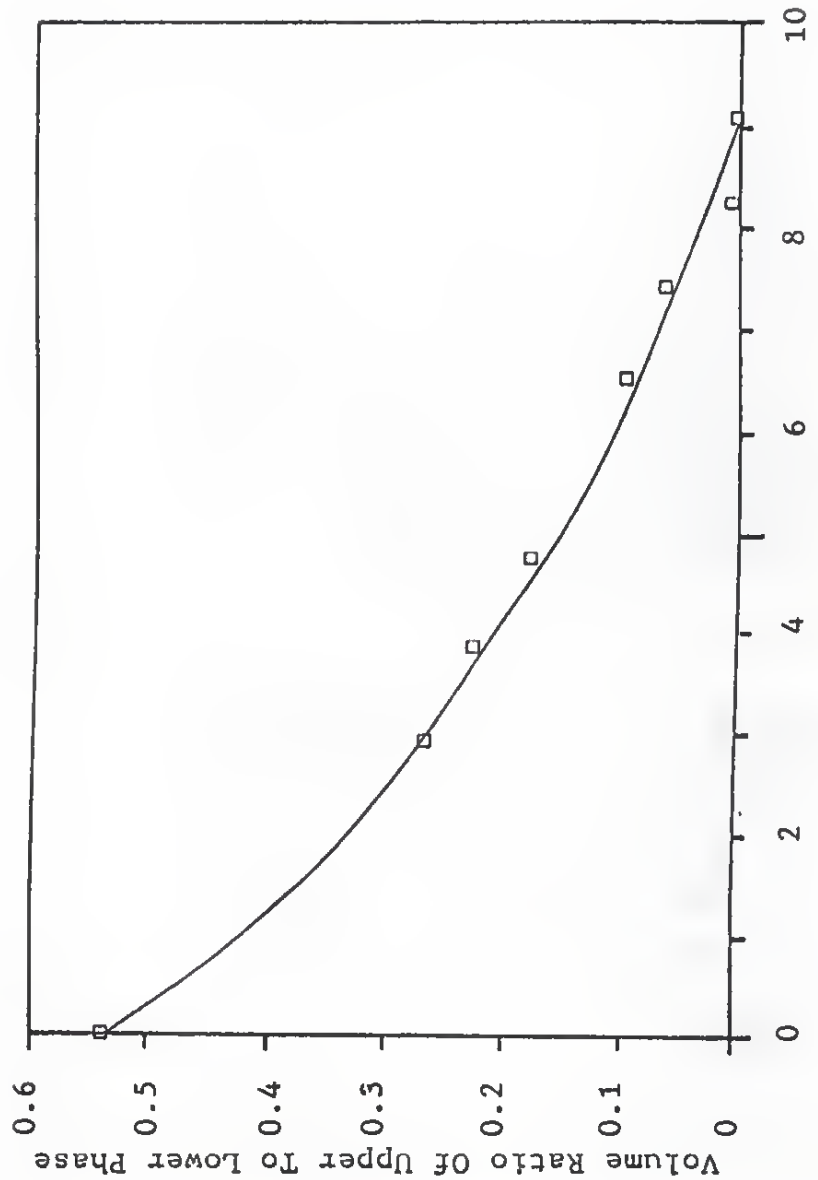


Figure 6-14. Effect of 2-butanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

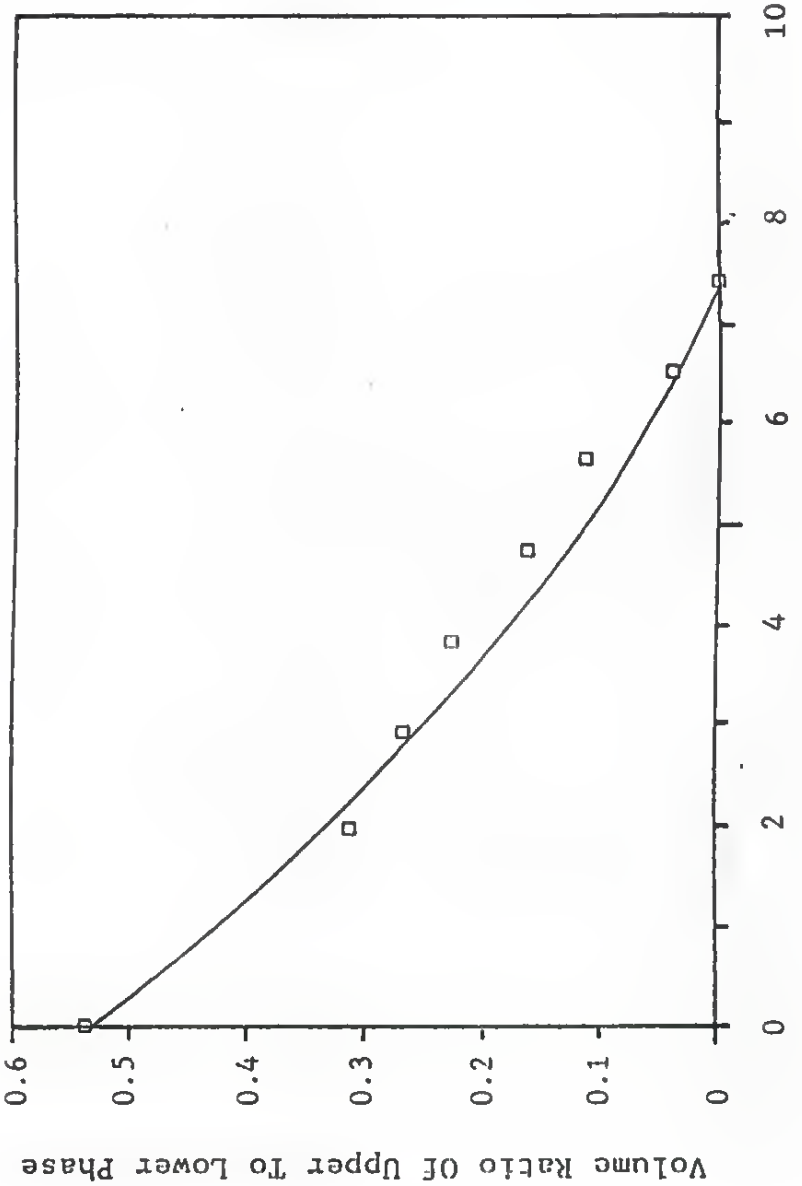


Figure 6-15. Effect of 3-pentanol on the stability of the methanol-isooctne-toluene mixture at -25^{0}C.

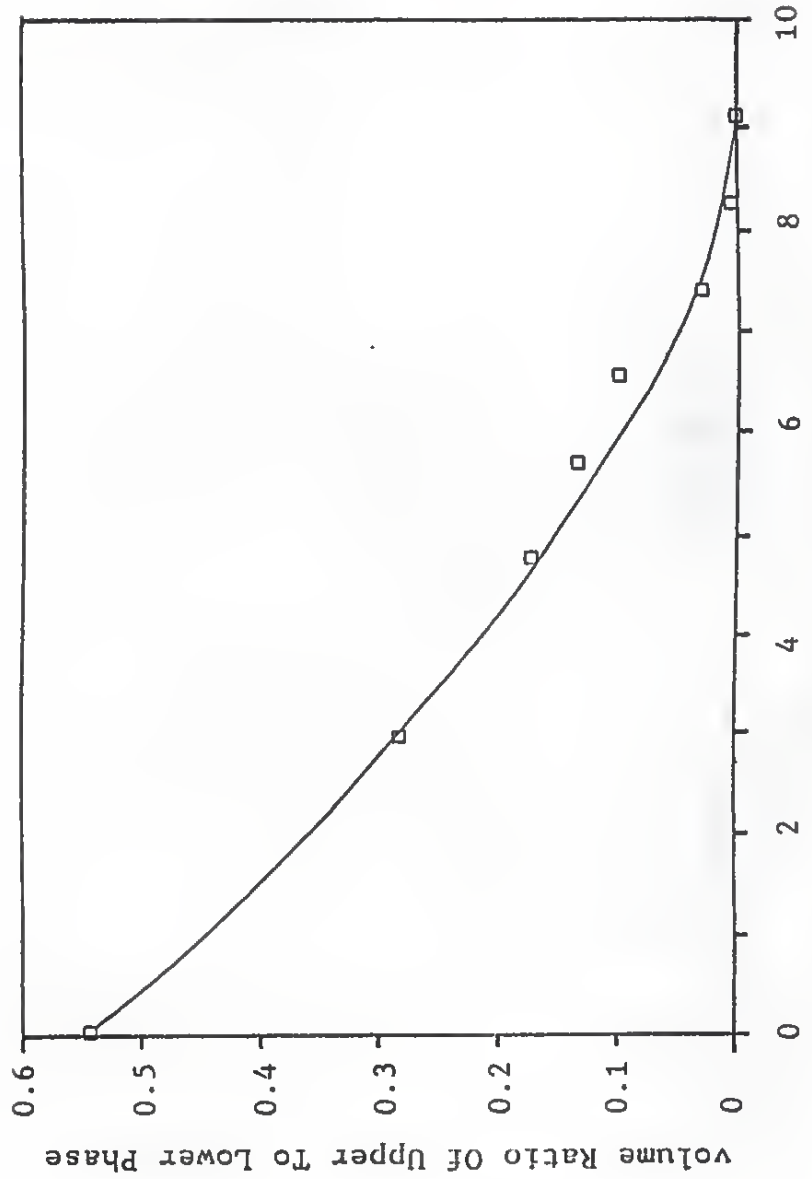


Figure 6-16. Effect of isoamyl alcohol on the stability of the methanol-isooctane-toluene mixture at -25°C.

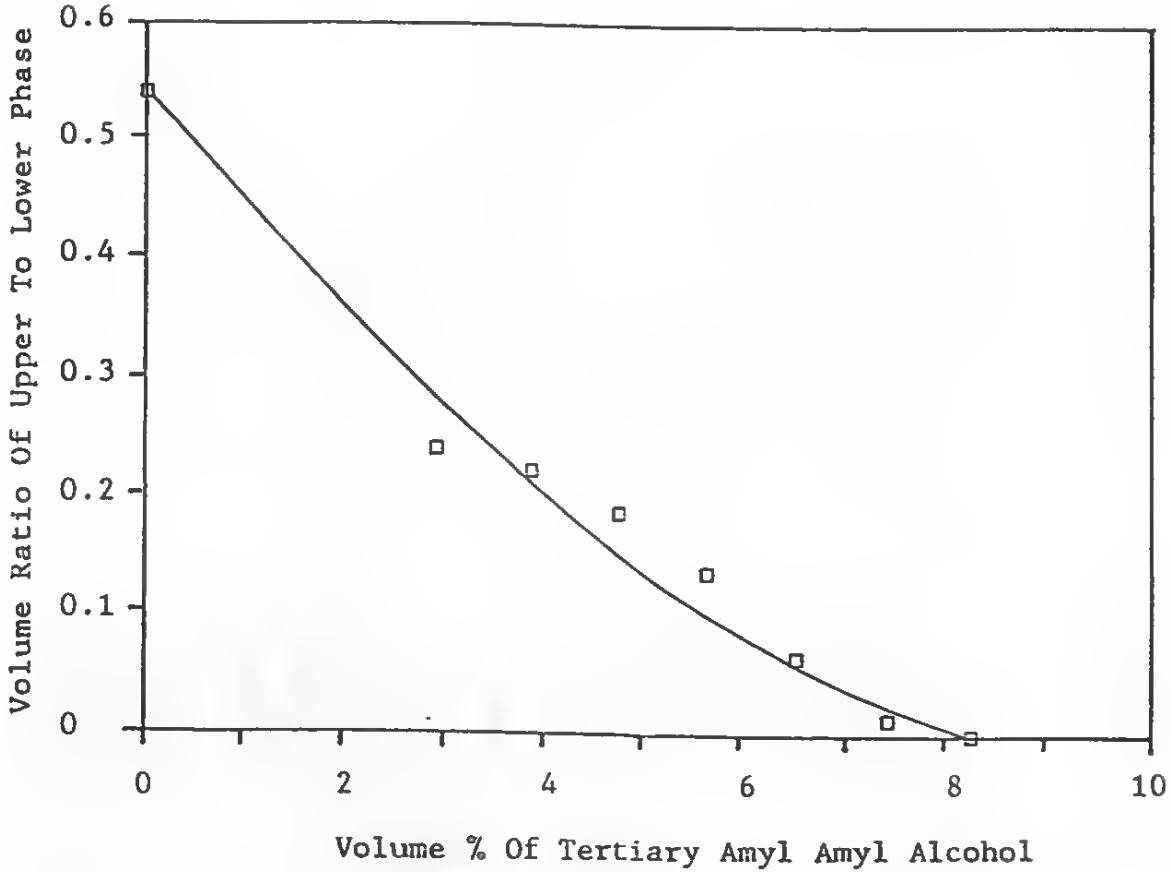


Figure 6-17. Effect of tertiary amyl alcohol on the stability of the methanol-isooctane-toluene mixture at -25°C.

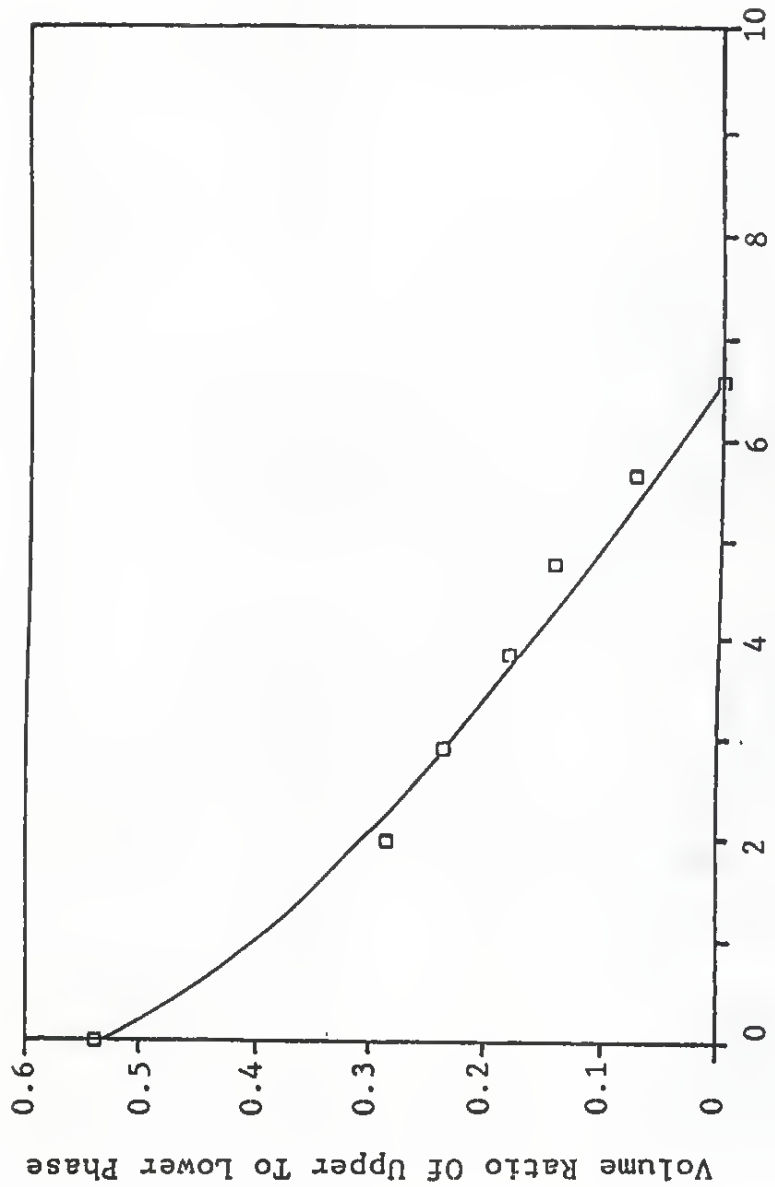


Figure 6-18. Effect of 2-hexanol on the stability of the methanol-isooctane-toluene mixture at $-25^{\circ}C$.

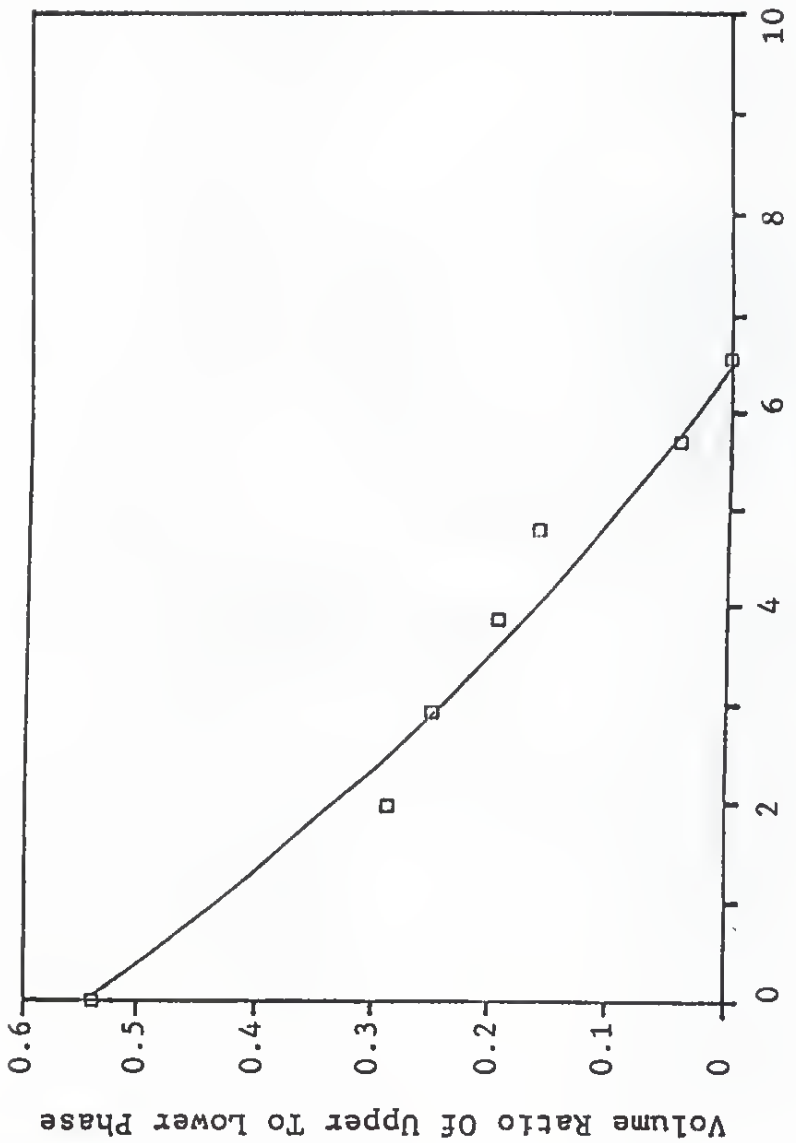


Figure 6-19. Effect of 4-heptanol on the stability of the methanol-isooctane-toluene mixture at $-25^{\circ}C$.

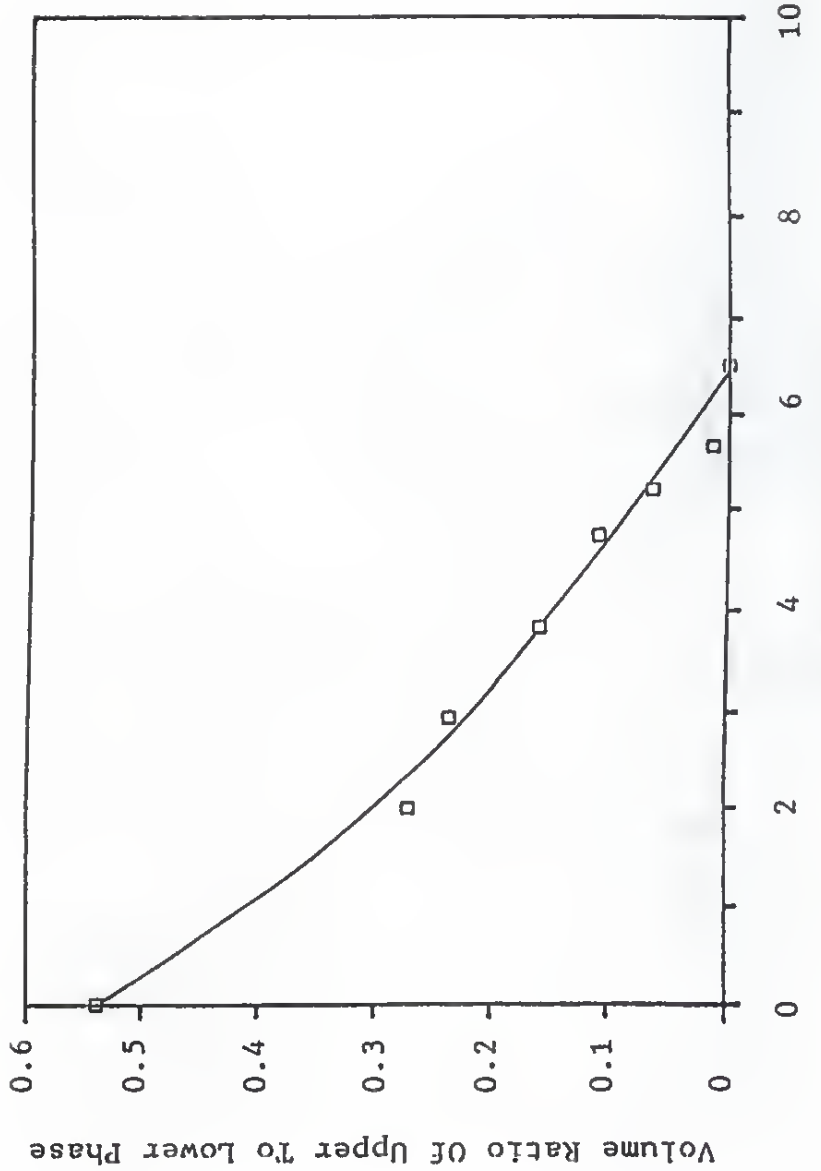


Figure 6-20. Effect of 2-octanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

being frozen. With other anionic surfactants, the mixture became frozen when the amount of the anionic surfactant exceeded about 4%. Therefore oleic acid was used to see the effect of the anionic surfactant alone on the phase stability of the mixture at -25°C. As shown in Figure 6-21, the effect of oleic acid was pronounced at the low concentration of oleic acid: the addition of about 0.5 % of oleic acid reduced the ratio of the upper to the lower phase from 0.54 to 0.31 compared to about 0.50 by the alcohols which can be seen from the previous Figures for the alcohols. The required amount of oleic acid to form the single phase at -25°C was 6.1%. This required amount of oleic acid was the same as that of normal heptanol to form the single phase at -25°C. Even though the mixture was frozen by addition of the used anionic surfactants except oleic acid, the mixture containing both anionic surfactant and alcohol was not frozen.

Table 6-3 and Figure 6-22 show the effect of the chain length of the anionic surfactant on the phase stability at -25°C. In this experiment, 0.1 ml of the anionic surfactant was added into the initial 10 ml of methanol-isooctane-toluene mixture before addition of normal pentanol. Like oleic acid, without normal pentanol, all the used anionic surfactant except palmitic acid reduced the upper to lower phase from 0.54 to about 0.31 compared to about 0.40 by the alcohols at 0.1% concentration. The mixture containing palmitic acid was frozen until the amount of normal pentanol increased to 2.9%. Like the alcohols, the required amount of normal pentanol to

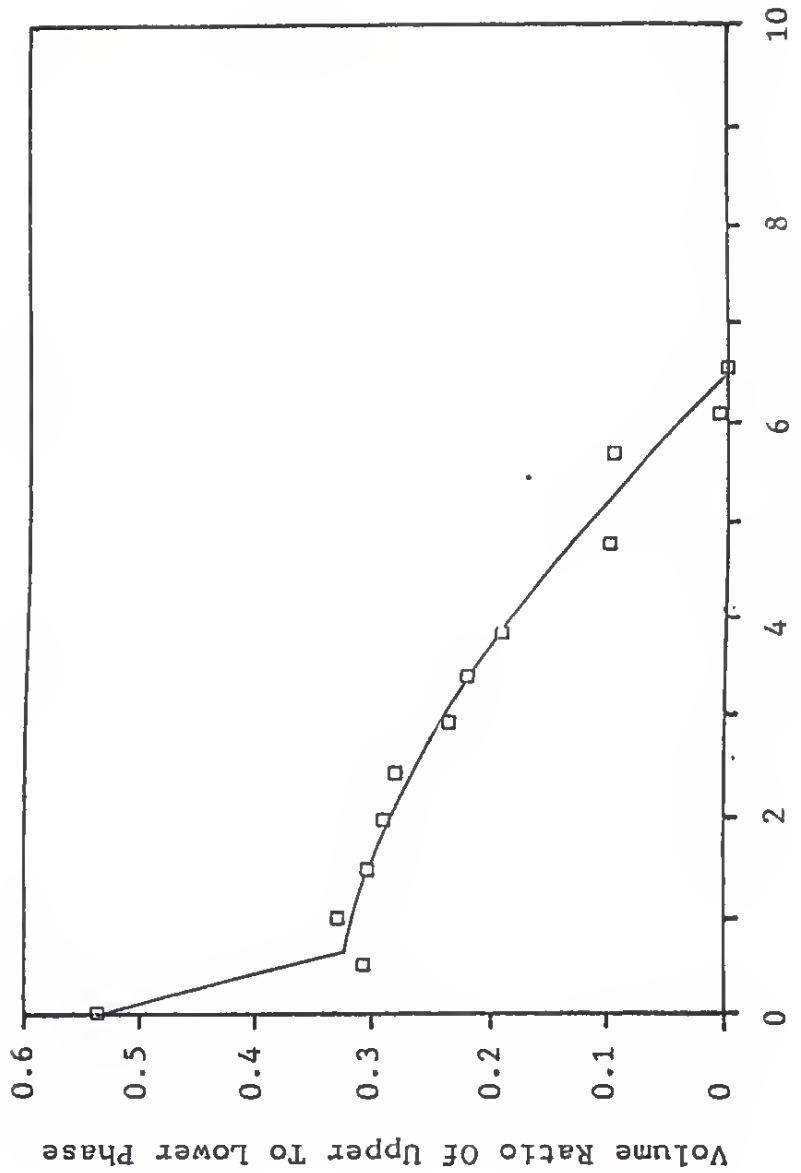


Figure 6-21. Effect of oleic acid on the stability of the methanol-isooctane-toluene mixture at -25°C.

Table 6-3. Required Amount of N-Pentanol to Form One Phase of 50% (v/v)Methanol-40%(v/v)Isooctane-10%(v/v)Toluene Mixture with Anionic Surfactant (0.01 ml/ml mixture) at -25 °C

Surfactants	Added N-Pentanol(Vol. %)	Total Added Additives(Vol. %)
No Surfactant	7.41	7.41
Lauric acid	6.48	7.41
Myristic acid	5.61	6.54
Palmitic acid	4.72	5.66
Oleic acid	5.61	6.54

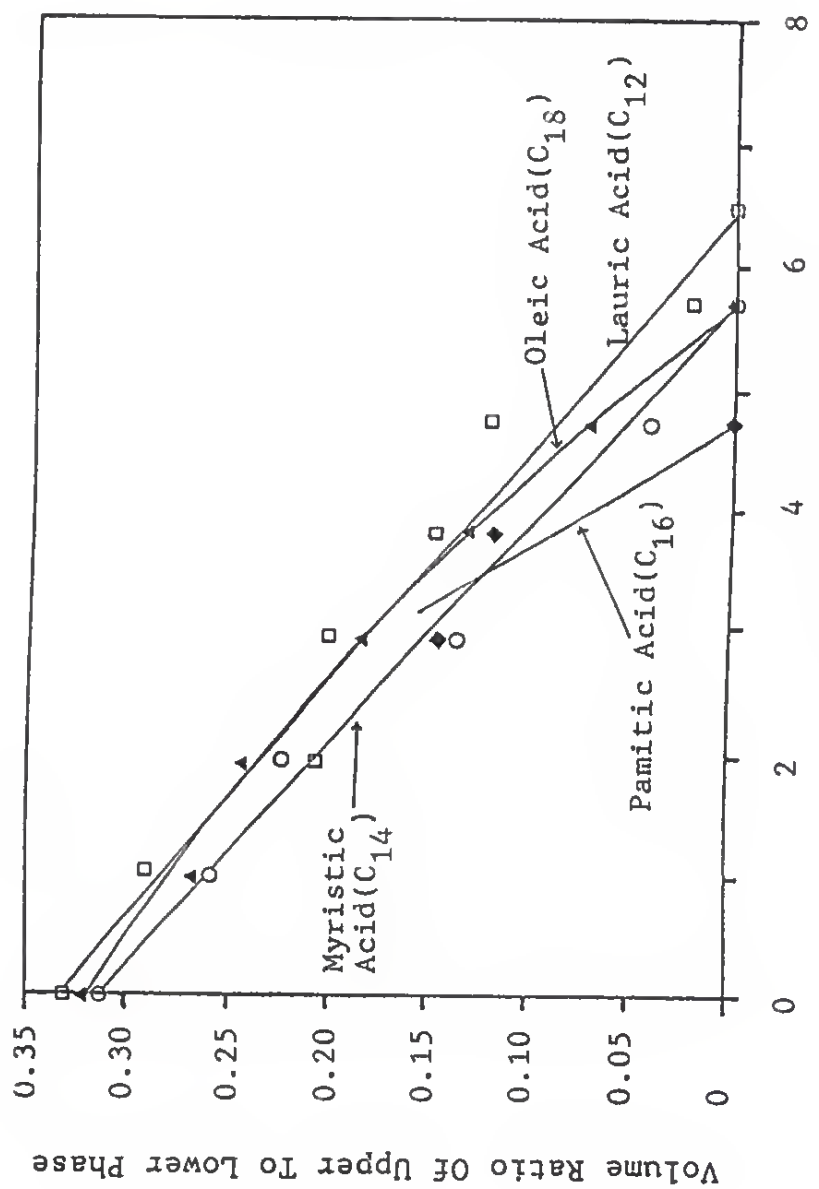


Figure 6-22. Effect of anionic surfactants on the stability of the methanol-isooctane-toluene mixture at -25°C.

form the single phase at -25°C decreased as the number of carbon atoma in the anionic surfactant increased. While the ratio of the upper to the lower phase decreased exponentially as a function of the alcohol concentration without the surfactant as seen before, the ratio decreased linearly as a function of the concentration of normal pentanol with the anionic surfactant except oleic acid. The required amount of normal pentanol for oleic acid was the same as that for myristic acid indicating that a double bond reduces the effectiveness. However, a double bond might introduced the fluidity into the system considering that the mixture with oleic acid alone was not frozen while the mixture with other acids were frozen without an alcohol. The addition of 1% of the anionic surfactant except lauric acid reduced the total required amount of the additives to form the single phase at -25°C compared to normal pentanol alone whose required amount was 7.4% as seen in Table 6-3.

Figure 6-23 shows the effect of the volume ratio of oleic acid to normal pentanol on the phase stability. The required amount of total additives to form the single phase at -25°C decreased as the ratio of oleic acid to normal pentanol increased. Remembering that the required amounts to form the single phase at -25°C were 7.4% for normal pentanol alone and 6.1% for oleic acid alone, the mixed additives of oleic acid and normal pentanol (5.6%) was most effective at the optimum ratio of oleic acid to normal pentanol, 2.0, as shown in Figure 6-24.

Table 6-4 shows the results from the nonionic surfactants. Unlike the anionic surfactants and the alcohols, the effect of the

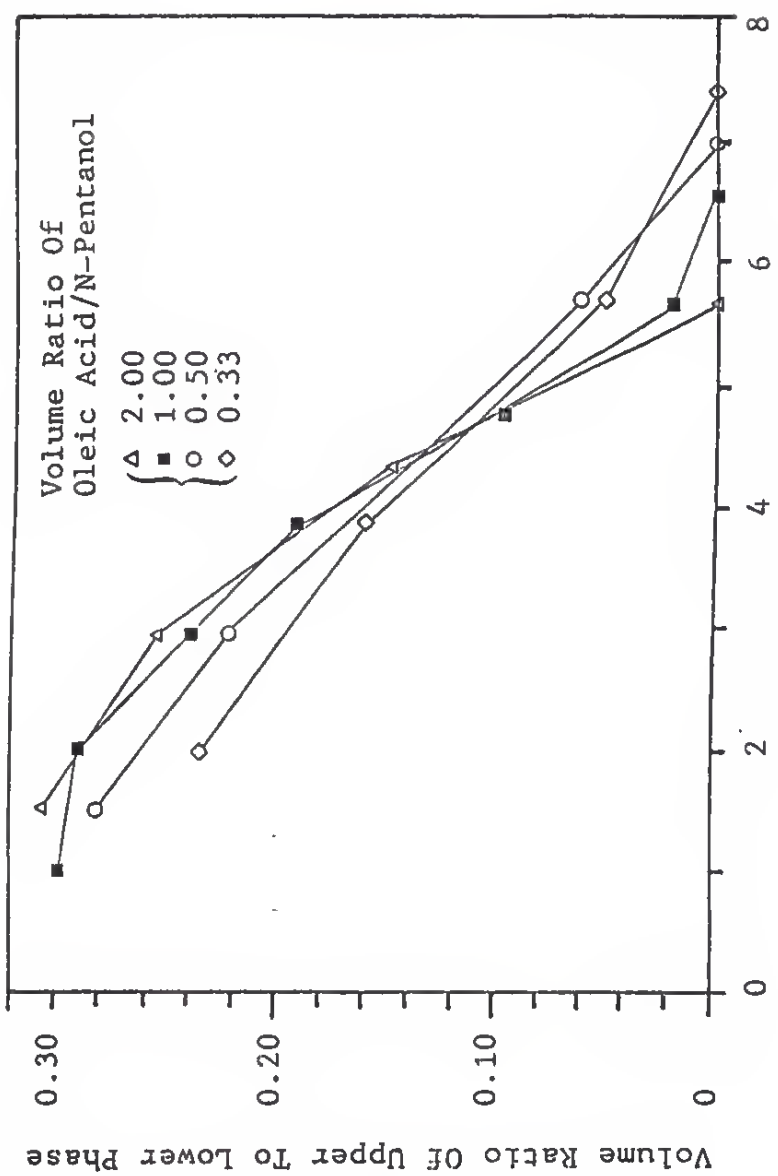


Figure 6-23. Effect of volume ratio of oleic acid to normal pentanol on the stability of the methanol-isooctane-toluene mixture at -25°C.

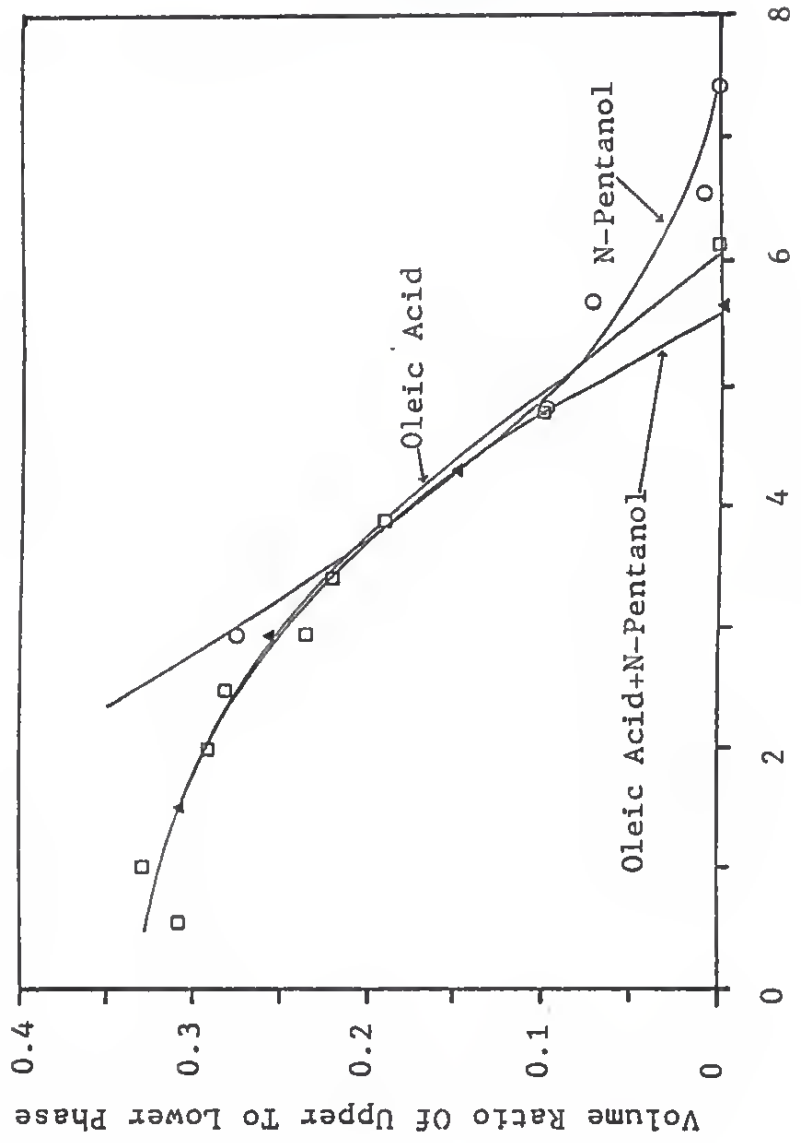


Figure 6-24. Effect of additives on the stability of the methanol-isooctane-toluenemixture at -25°C.

Table 6-4. Required Amount of N-Pentanol to Form One Phase of 50% (v/V)Methanol-40%(v/v)Isooctane-10%(v/v)Toluene Mixture with Nonionic Surfactant (0.01 ml/ml mixture)

Surfactants	HLB Value	Added N-Pentanol (Vol. %)	Total Added Additives (Vol. %)
No Surfactant		7.41	7.41
Arlacel 186	2.8	6.05	6.98
Arlacel 83	3.7	5.61	6.54
Brij 30	9.7	6.05	6.98
Brij 30sp	9.7	5.61	6.54
Tween 81	10.0	6.48	7.41
CO 520	10.0	6.05	6.98

structure of the surfactant could not be seen even though the nonionic surfactants having much different structure were chosen indicated from the range of HLB values from 2.8 to 10.0. Further, no used nonionic surfactant was more effective than the used anionic surfactants.

6.6 Discussions

Two immiscible liquids become miscible upon the addition of a proper third component in a certain range of temperature and concentration. The third component can be a cosolvent which can be miscible with both liquids. In this case, the resulting mixture is considered as the molecular solution in which each components are molecularly dispersed. Or, the third component can be a surface active agent such as a surfactant and an alcohol (15, 71, 109, 259-263). In this case, the resulting mixture is considered as a microemulsion because of the associated structures formed by the surface active agent and alcohol. Therefore, it is interesting to determine whether the stabilized mixture at $-25^{\circ}C$ represents a molecular solution or a microemulsion? Even though there is no evidence at present that the mixture is a microemulsion, the possibility that the mixture in this study was a microemulsion exists considering the following findings from the previous studies: 1) the mixed fuel consisting of aqueous ethanol and hydrocarbon fuels including a vegetable oil formed the hydrocarbon fuel-aqueous ethanol microemulsion by the addition of a surfactant even with the

water as small as 0.05% (191, 193); 2) the waterless microemulsion could be prepared by using methanol as well as other solvents such as glycerol, formamide, glycol, etc. in place of water (253); and 3) the solubility of oil in the microemulsion considerably increased if the light organic solvents, especially aromatics such as toluene and benzene, waa added to the system (126, 216, 264).

While it should be found through the future study whether the mixture in this study was a molecular solution or a microemulsion, the phase equilibrium data as shown in Table 6-5 suggest that, if the mixture was a microemulsion, the microemulsion was isooctane-in-methanol based on the following reasons: 1) the lower phase grew to become a single phase as the amount of the additive (normal pentanol) increased; 2) the amounts of the additive and methanol in the upper phase were too small to be detected indicating that the upper phase consisted of almoat pure hydrocarbons; 3) methanol was in the lower phase indicating that methanol might act aa water; and 4) toluene might increased the solubility of isooctane in the isooctane-in-methanol microemulsion.

6.7 Conclusions

The mixture consisting of 50% methanol, 40% isooctane, and 10% toluene by volume was a single phaae at room temperature. The mixture was, however, separated as two phases at the low temperatures. Thia study showed that the additives could stabilize the mixture as a single phase even at -25 °C. Further, the effect of the structure of the additives on the phase stability at -25 °C were

Table 6-5. Equilibrium Compositions of Two-Phase Methanol-Isooctane-Toluene Mixture at -25 °C Depending on Amount of Added N-Pentanol

Added N-Pentanol (Vol.%)	Upper Phase		Lower Phase			
	Isooctane (Vol.%)	Toluene (Vol.%)	Isooctane (Vol.%)	Toluene (Vol.%)	Methanol (Vol.%)	N-Pentanol (Vol.%)
0.0	31.7	3.3	8.3	6.7	50.0	0.0
2.0	20.5	2.0	18.7	7.8	49.0	2.0
2.9	17.0	1.5	21.8	8.3	48.5	2.9
3.8	10.9	0.7	27.6	8.9	48.1	3.8
6.5	3.7	0.1	33.7	9.3	46.7	6.5
7.4	0.0	0.0	37.0	9.3	46.3	7.4

a. The total volume of upper and lower phase is considered to be 100%. The volume % of each component in the the table refers to the total volume as 100%.

investigated. The conclusions from this study can be summarized as follows:

1. All the additives used in this study such as surfactants and alcohols kept the mixture as a single phase even at $-25^{\circ}C$ when the amount of the additive was large enough.
2. The required amounts of the used additives to form the single phase mixture at $-25^{\circ}C$ decreased as the chain length of the additive increased except for the branched alcohols and nonionic surfactants.
3. The required amount of the alcohol did not decreased further when the number of carbon atoms reached 6 and 8 for normal alcohols and secondary alcohols, respectively.
4 The required amounts of the normal alcohols were less than those of the corresponding secondary and branched alcohols.
5. The addition of the anionic surfactant decreased the required amounts of the additives.
6. Double bond of the anionic surfactant was less effective than the saturated anionic surfactant, but it seemed to introduce fluidity into the mixture.
7. The mixed additives of the anionic surfactant and the alcohol showed an optimum ratio of the surfactant to the alcohol at which the mixed additive was most effective.
8. The effectiveness of the additive(s) in this study decreased in the following order: the mixed additive of the anionic surfactant and the alcohol > the anionic surfactant > the alcohol.

9. The lower phase grew to become a single phase as the amount of the additive(s) increased.
10. The phase equilibrium data suggested that the mixture stabilized as a single phase at -25 ^{o}C by the addition of the additive was presumably isooctane-in-methanol microemulsion.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Effect of Nonionic Surfactants on Solubilization Capacity, Interfacial Tension, and Oil Displacement Efficiency of Microemulsions

W/O- and middle-phase microemulsions were prepared using nonionic surfactants as cosurfactants, rather than short-chain alcohols (alcohol-free microemulsions).

The alcohol-free w/o microemulsions prepared by AOT, Arlacel 20, mineral oil and water showed that its solubilization capacity for water depended on the weight ratios of two surfactants. The optimum weight ratio of two surfactants was AOT/Arlacel 20 = 0.48 at which the solubilization of water in the microemulsion was maximum, 0.83 of the volume ratio of water to oil. The great solubilization of water at the optimal weight ratio of surfactants implied that the substitution of a short-chain alcohol by a proper nonionic surfactant could increase the solubilization capacity of the microemulsion, resulting in low interfacial tension even with heavy oil. The oil displacement efficiency depended on the solubilization capacity of the microemulsion, as expected, because it is known that interfacial tension is a function of solubilization. A mechanism of oil displacement by alcohol-free w/o microemulsions was proposed and qualitatively supported by oil

displacement experiments: the more piston-like displacement for the optimum ratio of surfactants due to the lower interfacial tension, and the leaky piston displacement for the ratios of surfactants at which the solubilization of water was less than optimum. The effect of salt on oil displacement could be minimized by using fresh water during tertiary oil recovery.

The concept of the alcohol-free w/o microemulsion was extended to alcohol-free middle-phase microemulsion. The alcohol-free middle-phase microemulsion was formulated by TRS10-80, Tween 81, mineral oil and brine. The optimal salinity of thia microemulsion (2.63% NaCl) was almost the same as that of the microemulsion (2.80% NaCl) prepared by subatitution of Tween 81 with normal butanol. Measurements of solubilization and interfacial tension showed that the substitution of a short-chain alcohol by a proper nonionic surfactant again increased solubilization in the middle-phase microemulsion by 8 times at optimal salinity, resulting in lower interfacial tension by an order of magnitude than that of the middle-phase microemulsion containing short-chain alcohol. This was conaistent with the results from the previous alcohol-free w/o microemulsions.

The increased solubilization by substitution of a short-chain alcohol with a nonionic surfactant waa a reault of the increased average interaction energies between the surfactant and oil or water. Oil displacement experiments showed that the alcohol-free middle-phase microemulsion was much more effective for heavy oil recovery than middle-phase microemulsion containing a short-chain

alcohol due to much higher solubilization of heavy oil and brine, lower IFT and a higher viscoaity in the presence of nonionic surfactant.

7.2 Excluded Volume Effect of Anionic polymers on Anionic Surfactant Solutions

The addition of a surfactant in a polymer solution is known to decrease the interfacial tension. However, the mechanism to achieve low interfacial tenaion was suggested to differ depending on the combination of surfactant and polymer (a nonionic polymer-ionic surfactant or an anionic polymer-anionic surfactant system). Differences in the pattern of the surface tension change depending on the concentration of the surfactant between two systems were diacussed in favor of the proposed mechanism by Desai (116), that being an excluded volume effect of a polymer for the similarly charged system.

The excluded volume by polymer molecules was obtained from the second virial coefficient using SLS technique and the effective concentration of a aurfactant was calculated based on the obtained the excluded volume of polymer moleculea. This effective concentration was utilized to obtain the aurface and interfacial tensiona of the anionic polymer-anionic surfactant solution from the data of the aurface and interfacial tensions of the surfactant solutiona containing no polymer. The obtained valuea of aurface and interfacial tensions were matched well with the experimental data confirming the proposed mechanism of the excluded volume effect of a

polymer for the similarly charged systems. The values of IFT and surface tension obtained from the effective diameter of the polymer molecule were too large compared to the experimental values. This suggests that the excluded volume of the polymer is not only the physical volume of the polymer coils but it also includes the volume unavailable to surfactant due to exclusion forces.

Oil displacement efficiency were determined using polymer-surfactant solution, polymer solution alone, and surfactant solution alone. As expected, a small amount of the surfactant (0.02 wt.%) in the polymer solution dramatically increased oil recovery (75%) compared to the polymer solution (33%) and the dilute surfactant solution (15%) because of the low interfacial tension and the proper mobility control.

7.3 Thermal Conductivity of Microemulsions

A transient method to measure thermal diffusivity of liquid was developed. It is simple and inexpensive to construct, but it requires a large amount of sample and a long experimental time. The effect of the microstructure on the thermal diffusivity of the liquid was investigated. By changing the concentration of NaCl from 0.5 to 1.5 wt.% in the aqueous solution of TRS10-80 and isobutanol, the solution changed from an isotropic state to a birefringent state. While small differences of the salt concentration should not influence on thermal diffusivities of the brine, the thermal diffusivity of the isotropic solution was 20% larger than that of

the birefringent solution, indicating the strong influence of microstructure of the liquid on thermal diffusivitiy of the liquid.

Since the microemulsion has the unique microstructure compared to the usual liquid mixtures, thermal conductivity of microemulsions waa inveatigated by meaauring heat capacity and denaity in addition to thermal diffusivity. As expected, thermal conductivity of the w/o microemulsion increased with the increased amount of water solubilized in the microemulsion. Several known equations for thermal conductivity of a liquid mixture were used to fit the experimental data for the w/o microemulsion. One of the equations proposed for macroemulsion were reasonably useful for the microemulsions we examined; the equations for the liquid mixtures were not useful. The power law was very poor when the value of -2 was used for the parameter. Considering that the usual liquid mixtures require a value of -2, it is evidence that the structure of the microemulsion is considerably different from that of the molecularly mixed liquids.

7.4 Stability of Hydrocarbon and Alcohol Mixtures at -25°C

The effect of additives on the stability of a methanol-isooctane-toluene system waa investigated at -25°C. The addition of any additive such as an alcohol and a surfactant stabilized the mixture as a single phase at -25°C if the amount of the additive was large enough, while the mixture without any additive was separated as two phases even at 0°C. For both alcohols and surfactants except nonionic surfactanta, the required amount of the additive to form a

single phase decreased as the number of carbon atoms of additive increased. In the case of normal alcohols, this effect of chain length disappeared for alcohols having more than 8 carbon atoms. The normal alcohols were more effective than the corresponding secondary and the branched alcohols. For anionic surfactants, the saturated surfactants were more effective than the unsaturated surfactants. It was found that mixed additives of anionic surfactant and alcohol was most effective if their mixed ratio was optimum. The effectiveness of the additives used in this study was found to decrease in the following order: the mixed additive at the optimum ratio > anionic surfactant > alcohols. The possibility that the mixture stsbilized by additive was a waterless microemulsion was discussed. Gas chromatographic analysis suggested that the mixture stabilized by the additive at $-25^{\circ}C$ was presumably an isooctane-in-methanol microemulsion.

7.5 Recommendations for Further Studies

A study of the structural effects of nonionic surfactants on the solubilization capacity of the alcohol-free microemulsions is recommended using a series of nonionic surfactants having different head and tail groups with both light and heavy oils. The study will provide a basis to optimize the alcohol-free microemulsions. In particular, the study of the nonionic surfactants having the branched tails and a large head group will reveal whether a proper nonionic surfactant can replace the short-chain alcohol by

introduction of enough fluidity into the system. The results of the study can be utilized to formulate microemulsions in areas such as drugs, cosmetics, lubrication, oil recovery, and so on where the volatile and odorous characteristics of a short-chain alcohol are not desirable.

From Chapter 4, it is evident that the excluded volume effect of the polymer resulted in a reduction of the interfacial tension of the studied anionic polymer-anionic surfactant systems. Since the most of the studies were done with the commercial surfactants, it is desirable to repeat them with the pure surfactants. Further, the study of viscosity changes for such pure component systems will add the clue of the proposed mechanism because the intrinsic viscosity of the polymer solution will change if the conformation of the polymer is changed due to complex formation. In addition, the structural effects of both nonionic and cationic polymer require further study, to confirm the proposed mechanism and find the basis for formulating an optimum polymer-surfactant system under given conditions. The results of such a study may make use of surfactants in enhanced oil recovery both feasible and practical in the near future even at the current low price of oil because of the small amount of surfactant required for the oil recovery process.

A study of the thermal conductivity of pure surfactant solutions as a function of concentration is desirable. Since physical properties such as viscosity, surface tension, and electrical conductivity changed with the increase in surfactant concentration until micelles are formed, the future study on the

thermal properties of micellar solutions should reveal abrupt change at near cmc. For industrial applications, the alcohol-free w/o microemulsion can be used as a cutting fluid because evaporation of water can remove the generated heat effectively while the oil serves as a lubricant. In addition, w/o microemulsion can be changed to a waterless microemulsion which accommodates a cooling or heating medium such as glycerol and glycol to be used as a heat transfer fluid at low and moderate temperatures. Therefore, it is recommended to study the formulation of waterless microemulsions and their thermal conductivities.

While hydrocarbon mixtures such as methanol-isooctane-toluene offer promise as a future fuel, phase stability at low temperature is a problem. To understand the phase stability and to optimize the concentration of additive, it is necessary to identify the microstructure of the stabilized mixture by additives. QELS technique may be employed at the low temperatures to delineate the microstructure of these systems. In support of QELS technique, viscosity and electrical resistance can be studied. Further, the complete study of the phase equilibrium is recommended to complete the phase diagram of methanol-isooctane-toluene system.

APPENDIX

SOLUTION PROCEDURE FOR THE HEAT CONDUCTION OF A SPHERE

In Chapter 5, the governing equation and its boundary conditions for the heat conduction problem of a sphere were:

$$(1/r)\,[\delta^2(rT)\,/\,\delta r^2] = (1\,/\,\alpha)\,(\delta T\,/\delta\, t) \qquad (5\text{-}1)$$

$$T(r,\,0) = T_o \qquad 0 < r < R \qquad (5\text{-}2)$$

$$T(R,\,t) = T_1 \qquad t > 0. \qquad (5\text{-}3)$$

By substituting rT by U, equations 5-1, 5-2, and 5-3 become:

$$\delta^2 U\,/\,\delta r^2 = (1\,/\,\alpha)\,(\delta U\,/\,\delta\, t) \qquad (A1)$$

$$U(0,\,t) = 0 \qquad t > 0 \qquad (A2)$$

$$U(R,\,t) = R\,T_1 \qquad t > 0 \qquad (A3)$$

$$U(R,\,0) = r\,T_o \qquad 0 < r < R. \qquad (A4)$$

Now, U consists of two solutions: U = V + W where V is the solution for the steady state and W is the solution for the unsteady state, that is, $\lim_{t \to \infty} U = V$.

First find the steady-state solution, V. When t becomes infinite, equations A1, A2, A3, and A4 become:

$$d^2V\,/\,dr^2 = 0 \qquad (A5)$$

$$V(0) = 0 \qquad (A6)$$

$$V(R) = R\ T_1. \tag{A7}$$

From (A5), $V(r) = Ar + B$ (A8)

where A and B are arbitrary constants. A and B are found by solving the following equations simultaneously:

$$V(0) = 0 = B \tag{A9}$$

$$V(R) = A\ R + B = R\ T. \tag{A10}$$

Therefore, $A = T_1$ and $B = 0$. Finally, the steady-state solution is

$$V(r) = T_1\ r \tag{A11}$$

Since $U(r, t) = V(r) + W(r, t)$, (A12)

by substituting the equations A11 and A12 into equations A1, A2, A3, and A4,

$$\delta^2 W / \delta r^2 = (1 / \alpha)\ (\delta W / \delta t) \tag{A13}$$

$$W(0, t) = 0 \qquad t > 0 \tag{A14}$$

$$W(R, t) = 0 \qquad t > 0 \tag{A15}$$

$$W(r, 0) = r\ (T_o - T_1) = g(r) \qquad 0 < r < R. \tag{A16}$$

To apply the separation of variables method, let $W(r,t) = X(r)Y(t)$. Then equation A13 becomes:

$$X'' Y = (1 / \alpha) X Y' \tag{A17}$$

$$(X'' / X) = (1 / \alpha) (Y' / Y) = -\beta^2 \tag{A18}$$

where β = a positive constant. From equations A14, A15, and A18,

$$X'' + \beta^2 X' = 0 \tag{A19}$$

$$X(0) = 0 \tag{A20}$$

$$X(R) = 0. \tag{A21}$$

The solution is $X_n = \text{SIN}\, \beta_n r$ where $\beta_n = n\pi / R$ $(n = 1,2,3, \ldots)$. From equation A18,

$$Y' + \alpha \beta^2 Y = 0 \tag{A22}$$

The solution is $Y_n = \text{EXP}\, (-\alpha \beta_n^2 t)$. Since $W = X Y$, the solution, W, is:

$$W(r, t) = \sum_{n=1}^{\infty} \text{EXP}(-\alpha\beta_n^2 t)\, [1/N(\beta_n)]\, X(\beta_n, r) \times \int_0^R X(\beta_n, r')\, g(r')\, dr' \tag{A23}$$

where $1 / N(\beta_n) = 2 / R$,

$X(\beta_n, r) = \text{SIN}\ \beta_n r$

and $g(r) = r (T_o - T_1)$.

Therefore,

$$W(r,t) = 2(T_0-T_1)/R \sum_{n=1}^{\infty} (-R^2/n\pi)(-1)^n(\text{SIN } \beta_n r) \times \text{EXP } (-\alpha \beta_n^2 t). \quad \text{(A24)}$$

Since $U(r, t) = W(r, t) + V(r)$ and $T(r, t) = (1 / r) U(r, t)$,

$$\frac{T - T_1}{T_0 - T_1} = -(2R/\pi)(1/r) \sum_{n=1}^{\infty} (-1)^n(1/n)\text{SIN}(n\pi r/R) \times \text{EXP}(-(n\pi/R)^2 \alpha t). \quad \text{(5-4)}$$

To find $T(0, t)$,

$$\lim_{r\to 0} \frac{T - T_1}{T_0 - T_1} = \lim_{r\to 0} [-(2R/\pi) \sum_{n=1}^{\infty} (-1)^n(1/n)[\text{SIN}(n\pi r/R)/r] \times \text{EXP}[-(n\pi/R)^2 \alpha t]]. \quad \text{(A25)}$$

Since $\lim_{r\to 0} \frac{\text{SIN}(n\pi r/R)}{r} = \frac{n\pi}{R}$ by La' Hospital rule,

$$\lim_{r\to 0} \frac{T - T_1}{T_0 - T_1} = \left.\frac{T - T_1}{T_0 - T_1}\right|_{r=0} = -2 \sum_{n=1}^{\infty} (-1)^n \text{EXP}[-(n\pi/R)^2 \alpha t]. \quad \text{(5-5)}$$

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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